

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

**0 387 898  
A2**

12

## EUROPEAN PATENT APPLICATION

21 Application number: 90105008.8

51 Int. Cl.<sup>5</sup>: **G11B 7/24, G11B 7/26**

22 Date of filing: 16.03.90

30 Priority: 17.03.89 JP 63444/89  
17.03.89 JP 63445/89  
17.03.89 JP 63446/89  
17.03.89 JP 63447/89  
30.03.89 JP 76637/89

43 Date of publication of application:  
19.09.90 Bulletin 90/38

34 Designated Contracting States:  
**DE FR GB NL**

71 Applicant: **FUJI XEROX CO., LTD.**  
**No. 3-5, Akasaka 3-chome**  
**Minato-ku Tokyo 107(JP)**

72 Inventor: **Ueno, Osamu**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**  
Inventor: **Kobayashi, Hideo**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**  
Inventor: **Ueyanagi, Kiichi**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**

74 Representative: **Boeters, Hans Dietrich, Dr. et al**  
**Boeters & Bauer Patentanwälte**  
**Bereiteranger 15**  
**D-8000 München 90(DE)**

54 Optical recording medium.

37 An optical recording medium comprising a substrate having provided thereon a layer of a recording material whose optical properties reversibly change on application of light, heat, etc., to conduct recording, reproduction, or erasure of information is disclosed, wherein the recording material has a composition (i) to (vii) containing three or more kinds of elements specified in the specification. The optical recording material of the invention is capable of conducting rewriting of information at an increased speed and stably maintaining the recorded information for an extended period of time.

**EP 0 387 898 A2**

## OPTICAL RECORDING MEDIUM

FIELD OF THE INVENTION

5 This invention relates to a rewritable optical recording medium for recording, reproducing, and erasing information whose optical properties change on irradiation with a condensed light beam, such as a laser beam, to conduct recording, reproduction or erasure of information. More particularly, it relates to an improved optical recording medium with which rewriting of information can be carried out at an increased speed and the recorded information can be maintained stably for an extended period of time.

10

BACKGROUND OF THE INVENTION

15 Known rewritable optical recording media using a laser beam, etc. for recording information include magneto-optical recording media, and some of them have been put into practical use. An magneto-optical recording system comprises inverting magnetism of a recording layer by light energy and a magnetic field to conduct recording and detecting a difference of angle of Faraday rotation or angle of Kerr rotation due to the direction of magnetization to obtain reproduced signals. However, this system finds no practical method for conducting rewriting within one sector so that it has been of limited application.

20 On the other hand, a so-called phase transition type optical recording medium which utilizes a phase transition between a crystal phase and an amorphous phase has been proposed and receiving studies as another type of rewritable optical recording media. According to this recording system, rewriting within one sector can be carried out by using two light beams (i.e., recorded information is erased by the preceding beam, and recording is then effected with the beam following). When, in particular, a recording material  
25 requiring a short time for crystallization is employed, it is possible to conduct overwriting (simultaneous erasing and writing) with one light beam. Thus, the phase transition type recording medium is of wide application in many fields.

So far proposed recording materials applicable to the phase transition type optical recording media include a binary compound,  $\text{Sb}_2\text{Te}_3$ , and a ternary compound,  $\text{Ge-Sb-Te}$ , as disclosed in JP-A-63-225934 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). Recording is effected by irradiating a condensed light beam, such as a semi-conductor laser beam, on a recording layer comprising these materials to melt the irradiated part, followed by quenching to form an amorphous phase, while erasure is effected by irradiating the recorded part with a condensed light beam of a power lower than that used for recording to maintain the irradiated area at a crystallizing temperature for a  
35 given time to thereby return the amorphous phase to a crystalline phase.

In view of simplification of an optical system or improvement of a rate of transition, a recording material for use in the phase transition type optical recording media preferably has a short crystallizing time. Further, in view of long-term maintenance of recorded information, it is desirable that the recording material exhibits a stable amorphous phase.

40 In this connection, although the conventional recording material made of  $\text{Sb}_2\text{Te}_3$  has a short crystallizing time, i.e., satisfies the first requirement, it has insufficient stability in its amorphous phase so that the recorded information cannot be maintained for a long time.

On the other hand,  $\text{Ge-Sb-Te}$  disclosed in JP-A-63-225934 is synthesized by mixing  $\text{Sb}_2\text{Te}_3$  with  $\text{GeTe}$  which exhibits high stability in its amorphous phase but requires a long time for crystallization. What  $\text{Ge-Sb-Te}$  aims at is to exhibit properties midway between  $\text{Sb}_2\text{Te}_3$  and  $\text{GeTe}$  and thus to achieve both an  
45 increased rate of transition and improved preservation stability of recorded information. Nevertheless, since mixing of  $\text{GeTe}$  necessarily makes the crystallizing time longer than that of  $\text{Sb}_2\text{Te}_3$  alone, a sufficient rate of transition cannot be obtained.

50

SUMMARY OF THE INVENTION

An object of this invention is to provide a optical recording medium which exhibits stability in its amorphous phase and has a reduced crystallization time to thereby achieve rewriting of information at a

high speed and to stably maintain recorded information for a prolonged period of time.

The present invention relates to a optical recording medium comprising a substrate having provided thereon a recording layer consisting essentially of a recording material whose optical properties reversibly change on application of light, heat, etc., to conduct recording, reproduction, or erasing of information, wherein the recording material is:

(i) a recording material having a composition corresponding to a mixture of (i-a) a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element selected from Sn and Pb and the  $VI_b$  group element selected from S, Se, and Te and represented by chemical formula  $IV_bVI_b$  and (i-b) a  $V_bVI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from Sb, Bi, and As and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $V_bVI_{b3}$ , the composition containing at least one of Se and Te,

(ii) a recording material having a composition corresponding to a mixture of (ii-a) a congruent compound (which is a stoichiometric compound which does not decompose into other substances up to the melting point thereof) having a composition corresponding to a mixture of (ii-a-1) a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element selected from Sn and Pb and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $IV_bVI_b$  and (ii-a-2) a  $V_bVI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from Sb, Bi, and As and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $V_bVI_{b3}$  and (ii-b) the above-described  $V_bVI_{b3}$  type stoichiometric compound, the composition containing at least one of Se and Te,

(iii) a recording material having a composition corresponding to a mixture of (iii-a) a  $I_2VI_b$  type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $I_2VI_b$  and (iii-b) a multi-element stoichiometric compound composed of elements selected from at least two groups of the group  $III_b$  consisting of Ga, In, and Tl, the group  $IV_b$  consisting of Ge, Sn, and Pb, the group  $V_b$  consisting of As, Sb, and Bi, and the group  $VI_b$  consisting of S, Se, and Te, the composition containing at least one of Se and Te,

(iv) a recording material having a composition containing 3 or more kinds of elements and corresponding to a mixture of (iv-a) a  $III_bVI_b$  type stoichiometric compound composed of the group  $III_b$  element selected from Ga, In, and Tl and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $III_bVI_b$  and (iv-b) a multi-element stoichiometric compound composed of elements selected from at least two groups of the group  $III_b$  consisting of Ga, In, and Tl, the group  $IV_b$  consisting of Ge, Sn, and Pb, the group  $V_b$  consisting of As, Sb, and Bi, and the group  $VI_b$  consisting of S, Se, and Te, the composition containing at least one of Se and Te,

(v) a recording material having a composition containing 3 or more kinds of elements and corresponding to a mixture of (v-a) a  $III_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $III_b$  element selected from Ga, In, and Tl and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $III_{b2}VI_{b3}$  and (v-b) a multi-element stoichiometric compound composed of elements selected from at least two groups of the groups  $III_b$  consisting of Ga, In, and Tl, the group  $IV_b$  consisting of Ge, Sn, and Pb, and the group  $VI_b$  consisting of S, Se, and Te, the composition containing at least one of Se and Te,

(vi-1) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound (i.e., composed of three kinds of elements) having a composition corresponding to a mixture of (vi-1-a) a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element selected from Sn and Pb and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $IV_bVI_b$  and (vi-1-b) a  $V_bVI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from Sb, Bi, and As and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $V_bVI_{b3}$ , in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups  $IV_b$ ,  $V_b$ , and  $VI_b$  and Si and Ge of the group  $IV_b$ ,

(vi-2) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-2-a) a  $I_2VI_b$  type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $I_2VI_b$  and (vi-2-b) a  $V_bVI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from As, Sb, and Bi and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $V_bVI_{b3}$ , in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one

element selected from the above-described elements of the groups I, V<sub>b</sub>, and VI<sub>b</sub>.

(vi-3) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-3-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (vi-3-b) a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups I, III<sub>b</sub>, and VI<sub>b</sub> and Al of the group III<sub>b</sub>.

(vi-4) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-4-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (vi-4-b) a IV<sub>b</sub>VI<sub>b2</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b2</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups I, IV<sub>b</sub>, and VI<sub>b</sub> and Si of the group IV<sub>b</sub>.

(vi-5) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-5-a) a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub> and (vi-5-b) a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub>, IV<sub>b</sub>, and VI<sub>b</sub>, Al of the group III<sub>b</sub>, and Si of the group IV<sub>b</sub>.

(vi-6) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-6-a) a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub> and (vi-6-b) a IV<sub>b</sub>VI<sub>b2</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b2</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub>, IV<sub>b</sub> and VI<sub>b</sub>, Al of the group III<sub>b</sub>, and Si of the group IV<sub>b</sub>.

(vi-7) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of two kinds of a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub> and VI<sub>b</sub> and Al of the group III<sub>b</sub>.

(vi-8) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is S or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of two kinds of a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub> and VI<sub>b</sub> and Al of the group III<sub>b</sub>.

(vi-9) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having

a composition corresponding to a mixture of (vi-9-a) a  $\text{III}_b\text{VI}_b$  type stoichiometric compound composed of the group  $\text{III}_b$  element selected from Ga, In, and Tl and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{III}_b\text{VI}_b$  and (vi-9-b) a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound composed of the group  $\text{IV}_b$  element selected from Ge, Sn, and Pb and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{IV}_b\text{VI}_b$ , in which at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups  $\text{III}_b$ ,  $\text{IV}_b$ , and  $\text{VI}_b$ , At of the group  $\text{III}_b$ , and Si of the group  $\text{IV}_b$ , and

(vii) a recording material made of a solid solution composed of at least three elements selected from the group consisting of the group  $\text{III}_b$  element selected from Ga, In, and Tl, the group  $\text{IV}_b$  element selected from Ge, Sn, and Pb, the group  $\text{V}_b$  element selected from As, Sb, and Bi, and the group  $\text{VI}_b$  element selected from S, Se, and Te and containing at least one of Se and Te, the solid solution being synthesized from plural elements or stoichiometric compounds having the same crystal system.

The symbols "I,  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$ " as used herein means group numbers of the periodic table. The symbol "I" represents the subgroups  $\text{I}_a$  and  $\text{I}_b$ .

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-section showing a layer structure of the optical recording medium according to the present invention.

Figures 2 through 6 each illustrates a pseudo-binary phase diagram of the recording material used in Examples 1 to 5, respectively.

Figures 7 through 13 each illustrates a pseudo-binary phase diagram of the recording material used in Examples 6 to 12, respectively.

Figures 14 through 23 each illustrates a pseudo-binary phase diagram of the recording material used in Examples 13 to 22, respectively.

Figures 24 through 33 each illustrates a pseudo-binary phase diagram of the stoichiometric three-element compound before substitution used as a recording material in Comparative Example 2 and Examples 25 to 28 and 30 to 34, respectively.

Figures 34 through 41 each illustrates a pseudo-binary phase diagram of the recording material used in Examples 35 to 42, respectively.

### DETAILED DESCRIPTION OF THE INVENTION

#### Recording Materials (i) and (ii):

The  $\text{IV}_b\text{VI}_b$  type stoichiometric compound in recording materials (i) and (ii) includes SnS, SnSe, SnTe, PbS, PbSe and PbTe. The  $\text{V}_b\text{VI}_b$  type stoichiometric compound includes those composed of the same  $\text{V}_b$  elements and the same  $\text{VI}_b$  elements, e.g.,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , and  $\text{As}_2\text{Te}_3$ ; and those containing different  $\text{V}_b$  elements or different  $\text{VI}_b$  elements, e.g.,  $\text{Sb}_2\text{SeTe}_2$ ,  $\text{Bi}_2\text{SeTe}_2$ ,  $\text{Bi}_2\text{Se}_2\text{Te}$ , and  $\text{Bi}_2\text{STe}_2$ .

Recording materials (i) and (ii) which have a composition corresponding to a mixture of the  $\text{IV}_b\text{VI}_b$  type stoichiometric compound and the  $\text{V}_b\text{VI}_b$  type stoichiometric compound may be any of materials composed of at least three kinds of elements selected from the group consisting of the group  $\text{IV}_b$  elements (i.e., Sn and Pb), the group  $\text{V}_b$  elements (i.e., Sb, Bi, and As), and the group  $\text{VI}_b$  elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $\text{IV}_b\text{VI}_b$  type stoichiometric compound and the  $\text{V}_b\text{VI}_b$  type stoichiometric compound at an arbitrary mixing ratio. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture, and the total content of Se and Te in the recording material is preferably not less than 30 atomic% based on the total atoms constituting the recording material. Examples of such a composition include a composition consisting of three elements containing Se and/or Te, a composition consisting of four elements containing Se and/or Te, and compositions consisting of more than four elements (e.g., a five-element composition and a six-element composition).

Specific examples of recording materials of this type are mixtures composed of at least three elements

containing Se and/or Te which is obtained by mixing the  $IV_6VI_6$  type stoichiometric compound selected from SnS, SnSe, SnTe, PbS, PbSe, PbTe, etc. with the  $V_{b2}VI_{b3}$  type stoichiometric compound selected from  $Sb_2S_3$ ,  $Sb_2Se_3$ ,  $Sb_2Te_3$ ,  $Bi_2S_3$ ,  $Bi_2Se_3$ ,  $Bi_2Te_3$ ,  $As_2S_3$ ,  $As_2Se_3$ ,  $As_2Te_3$ ,  $Sb_2SeTe_2$ ,  $Bi_2SeTe_2$ ,  $Bi_2Se_2Te$ ,  $Bi_2STe_2$ , etc., at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $Sn_2Sb_2Se_5$ ,  $SnBi_2Te_4$ ,  $PbBi_4Se_7$ ,  $PbBi_2Se_4$ , and  $Pb_3Bi_4Se_9$ ; congruent compounds made of these mixtures, e.g.,  $Sn_2Sb_6Se_{11}$ ,  $SnSb_2Te_4$ ,  $Pb_2Sb_6Te_{11}$ , and  $PbBi_4Te_7$ ; solid solutions made of these mixtures, composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio. Further included are mixtures of the above-described congruent compound and the  $V_{b2}VI_{b3}$  type stoichiometric compound, e.g.,  $Sb_2S_3$ ,  $Sb_2Se_3$ ,  $Sb_2Te_3$ ,  $Bi_2S_3$ ,  $Bi_2Se_3$ ,  $Bi_2Te_3$ ,  $As_2S_3$ ,  $As_2Se_3$ ,  $As_2Te_3$ ,  $Sb_2SeTe_2$ ,  $Bi_2SeTe_2$ ,  $Bi_2Se_2Te$ , and  $Bi_2STe_2$ , at an arbitrary mixing ratio.

Use of recording material (i) makes it possible to increase stability of the amorphous phase of the recording layer and to reduce the crystallization time of the recording layer.

Use of recording material (ii) makes it possible to increase stability of the amorphous phase of the recording layer and to reduce the crystallization time of the recording layer. In addition, there is formed no  $IV_6VI_6$  type stoichiometric compound having a high melting point at the time of phase transition between a crystal phase and an amorphous phase.

Reasons, which the inventors believe, for the reduction of the crystallization time of the above-described recording material layer as compared with the conventionally employed Ge-Sb-Te recording material layer are as follows. The  $IV_6VI_6$  type stoichiometric compound in recording materials (i) and (ii) has a melting point as shown in Table 1 below. The "melting point" as herein referred to means a temperature necessary for cutting all the atomic bonds forming the solid phase. With a crystal structure being the same, the melting point is considered to faithfully reflect the interatomic bond strength. Accordingly, as the melting point becomes higher, the crystal phase seems to have a higher interatomic bond strength. Because all the  $IV_6VI_6$  type stoichiometric compounds listed in Table 1 have an NaCl type crystal structure, the way of thinking stated above can be applied to these compounds. Although GeTe has a layered structure called a GeTe type or an As type at room temperature, it is transformed to the above-mentioned NaCl type at temperatures of 440 °C or higher so that the melting point of GeTe shown in Table 1 is regarded to the one for the NaCl type.

That is, seeing that the  $IV_6VI_6$  type stoichiometric compounds in recording materials (i) and (ii) have higher melting points than the melting point of GeTe, it is believed that the  $IV_6VI_6$  interatomic bond strength is higher than the Ge-Te interatomic bond strength in their crystal phase. Thus, in the recording material having a composition corresponding to a mixture of the  $IV_6VI_6$  type stoichiometric compound and the  $V_{b2}VI_{b3}$  type stoichiometric compound, the  $IV_6VI_6$  interatomic bond strength is strong, and the free energy in its crystal phase is low.

It is therefore assumed that the above-described recording materials show a greater difference in free energy between the crystal phase and the amorphous phase, i.e., a greater transition energy, as compared with the conventional Ge-Sb-Te recording material and, as a result, the crystallization time can be reduced.

On the other hand, the reason why the recording layer comprising recording material (i) or (ii) exhibits higher stability in its amorphous phase than the conventional  $Sb_2Te_3$  recording material is that recording material (i) or (ii) is a three or more element material having stronger inhibitory effects on atomic movement due to a difference in atomic radius and thus possesses a greater activation energy than two-element materials.

TABLE 1

$IV_6VI_6$ Type Compound	Melting Point (°C)
SnS	881
SnSe	860
SnTe	790
PbS	1103
PnSe	1076
PbTe	917
GeTe	725

Recording Material (iii):

5 The  $I_2VI_6$  type stoichiometric compound in recording material (iii) includes those containing the same group I elements, e.g.,  $Li_2S$ ,  $Li_2Se$ ,  $Li_2Te$ ,  $Na_2S$ ,  $Na_2Se$ ,  $Na_2Te$ ,  $K_2S$ ,  $K_2Se$ ,  $K_2Te$ ,  $Rb_2S$ ,  $Rb_2Se$ ,  $Rb_2Te$ ,  $Cs_2S$ ,  $Cs_2Se$ ,  $Cs_2Te$ ,  $Cu_2S$ ,  $Cu_2Se$ ,  $Cu_2Te$ ,  $Ag_2S$ ,  $Ag_2Se$ ,  $Ag_2Te$ ,  $Au_2S$ ,  $Au_2Se$ , and  $Au_2Te$ ; and those containing different group I elements, e.g.,  $CuAgS$ ,  $CuAgSe$ , and  $CuAgTe$ .

10 The multi-element stoichiometric compound is a stoichiometric compound composed of elements selected from at least two groups of the groups  $III_b$ ,  $IV_b$ ,  $V_b$ , and  $VI_b$ . Examples of such a multi-element stoichiometric compound include a  $V_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from As, Sb, and Bi and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $V_{b2}VI_{b3}$ ; a  $III_{b2}VI_{b3}$  type stoichiometric compound composed of the group  
15  $III_b$  element selected from Ga, In, and Tl and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $III_{b2}$  and a  $IV_bVI_{b2}$  type stoichiometric compound composed of the group  $IV_b$  element selected from Ge, Sn, and Pb and the group  $VI_b$  element selected from S, Se, and Te and represented by chemical formula  $IV_bVI_{b2}$ .

The  $V_{b2}VI_{b3}$  type stoichiometric compound includes those composed of the same group V elements  
20 and the same group  $VI_b$  elements, e.g.,  $Sb_2S_3$ ,  $Sb_2Se_3$ ,  $Sb_2Te_3$ ,  $Bi_2S_3$ ,  $Bi_2Se_3$ ,  $Bi_2Te_3$ ,  $As_2S_3$ ,  $As_2Se_3$ , and  $As_2Te_3$ ; and those containing different group  $V_b$  elements or different group  $VI_b$  elements, e.g.,  $Sb_2SeTe_2$ ,  $Bi_2SeTe_2$ ,  $Bi_2Se_2Te$ , and  $Bi_2STe_2$ .

The  $III_{b2}VI_{b3}$  type stoichiometric compound includes those containing the same group  $III_b$  elements and the same group VI elements, e.g.,  $Ga_2S_3$ ,  $Ga_2Se_3$ ,  $Ga_2Te_3$ ,  $In_2S_3$ ,  $In_2Se_3$ ,  $In_2Te_3$ ,  $Tl_2S_3$ ,  $Tl_2Se_3$ , and  
25  $Tl_2Te_3$ ; and those containing different  $III_b$  elements or different  $VI_b$  elements, e.g.,  $GaInS_3$  and  $In_2STe_2$ .

The  $IV_bVI_{b2}$  type stoichiometric compound includes  $GeS_2$ ,  $GeSe_2$ ,  $SnS_2$ , and  $SnSe_2$ .

Recording material (iii) which has a composition corresponding to a mixture of the  $I_2VI_6$  type stoichiometric compound and the multi-element stoichiometric compound may be any of materials composed of at least three elements selected from the group I elements (i.e., Li, Na, K, Rb, Cs, Cu, Ag, and  
30 Au), the group  $III_b$  elements (i.e., Ga, In, and Tl), the  $IV_b$  elements (i.e., Ge, Sn and Pb), the group  $V_b$  elements (i.e., As, Sb, and Bi), and the group  $VI_b$  elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $I_2VI_6$  type stoichiometric compound with a multi-element stoichiometric compound (e.g., a  $V_{b2}VI_{b3}$  type stoichiometric compound, a  $III_{b2}VI_{b3}$  type stoichiometric compound, and a  $IV_bVI_{b2}$  type stoichiometric compound) at an  
35 arbitrary mixing ratio. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture, and the total content of Se and Te in the recording material is preferably not less than 30 atomic% based on the total atoms constituting the recording material. Examples of such a composition include a composition consisting of three elements containing Se and/or Te, a composition consisting of four elements containing Se and/or Te, and compositions consisting of more  
40 than four elements (e.g., a five-element composition and a six-element composition).

Specific examples of recording material (iii) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $I_2VI_6$  type stoichiometric compound with a  $V_{b2}VI_{b3}$  type stoichiometric compound selected from  $Sb_2S_3$ ,  $Sb_2Se_3$ ,  $Sb_2Te_3$ ,  $Bi_2S_3$ ,  $Bi_2Se_3$ ,  $Bi_2Te_3$ ,  $As_2S_3$ ,  $As_2Se_3$ ,  $As_2Te_3$ ,  $Sb_2SeTe_2$ ,  $Bi_2SeTe_2$ ,  $Bi_2Se_2Te$ ,  $Bi_2STe_2$ , etc. at an arbitrary ratio;  
45 stoichiometric compounds made of these mixtures, e.g.,  $Sn_2Sb_2Se_5$ ,  $SnBi_2Te_4$ ,  $PbBi_4Se_7$ ,  $PbBi_2Se_4$ ,  $Pb_3Bi_4Se_9$ , etc.; congruent compounds made of these mixtures, e.g.,  $Sn_2Sb_6Se_{11}$ ,  $SnSb_2Te_4$ ,  $Pb_2Sb_6Te_{11}$ ,  $PbBi_4Te_7$ , etc.; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio.

50 Further included in recording material (iii) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $I_2VI_6$  type stoichiometric compound and a  $III_{b2}VI_{b3}$  type stoichiometric compound, e.g.,  $Ga_2S_3$ ,  $Ga_2Se_3$ ,  $Ga_2Te_3$ ,  $In_2S_3$ ,  $In_2Se_3$ ,  $In_2Te_3$ ,  $Tl_2S_3$ ,  $Tl_2Se_3$ ,  $Tl_2Te_3$ ,  $GaInS_3$ ,  $In_2STe_2$ , etc. at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $CuGaSe_2$ ,  $CuInSe_2$ ,  $CuInTe_2$ ,  $AgInTe_2$ , etc.; congruent compounds made of these mixtures,  
55 e.g.,  $AgGaSe_2$ ,  $AgIn_2Se_8$ , etc.; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio.

Furthermore included in recording material (iii) are mixtures composed of at least three elements

containing Se and/or Te which are obtained by mixing the above-described  $I_2VI_6$  stoichiometric compound with a  $IV_6VI_6$  type stoichiometric compound selected from  $GeS_2$ ,  $GeSe_2$ ,  $SnS_2$ ,  $SnSe_2$ , etc. at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $Cu_2SnSe_3$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary mixing ratio.

Use of recording material (iii) makes it possible to increase stability of the amorphous phase of the recording layer and to reduce the crystallization time of the recording layer.

Reason, which the inventors believe, for the reduction of the crystallization time of the above-described recording material layer as compared with the conventionally employed Ge-Sb-Te recording material layer is as follows.

Electronegativities of elements constituting the conventional recording materials and recording materials (iii) of the invention are shown in Table 2 below. The electronegativities herein referred to are values of Phillips' electronegativity which are obtained by adding the screening effect by valence electrons to the values of Pauling's electronegativity (see J.C. Phillips, Bonds and Bands in Semiconductors, Academic Press, New York and London (1973), with the exception that the values for K, Rb, and Cs are Pauling's electronegativities since Phillips' electronegativities for these elements have not yet been obtained. It is known that ionic character of an interatomic bond tends to increase as a difference in electronegativity between the atoms becomes greater.

The Phillips' electronegativities herein used are calculated values obtained for regular tetrahedral structures. Since the electron orbit in the atoms constituting recording material (iii), inclusive of a non-bonding pair, is regular-tetrahedral, it would be safe to apply the values of Phillips' electronegativity to these atoms.

TABLE 2

$I_a$	$I_b$	$III_b$	$IV_b$	$V_b$	$VI_b$
Li 1.00					
Na 0.72					S 1.87
K (0.8)*	Cu 0.79	Ga 1.13	Ge 1.35	As 1.57	Se 1.79
Rb (0.8)*	Ag 0.57	In 0.99	Sn 1.15	Sb 1.31	Te 1.47
Cs (0.7)*	Au 0.64	Tl 0.94	Pb 1.09	Bi 1.24	

\* Pauling's electronegativities

Interatomic bonds in the conventional Ge-Sb-Te being considered, the Phillips' electronegativity values of Ge, Sb, and Te are 1.35, 1.31, and 1.47, respectively, as shown in Table 2, giving a difference of 0.04 between Ge and Sb, 0.16 between Sb and Te, and 0.12 between Ge and Te. Thus, it can be seen that ionic bond strength of Ge-Sb, Sb-Te and Ge-Te bonds constructing Ge-Sb-Te is weak.

In the  $I_2VI_6$  type stoichiometric compound constituting a part of recording material (iii), to the contrary, a difference in electronegativity between Te whose electronegativity is the lowest (1.47) of the group  $VI_b$  elements and Li whose electronegativity is the highest (1.00) of the group I elements is 0.47. On the other hand, a difference between S whose electronegativity is the highest (1.87) of the group  $VI_b$  elements and Ag whose electronegativity is the lowest (0.57) of the group I elements is 1.30. That is, the electronegativity difference between the group I elements and the group  $VI_b$  elements widely ranges from 0.47 to 1.30, indicating strong ionic bond strength between the group I atom and the group  $VI_b$  atom.

From these considerations, it is believed that the group I atom-group  $VI_b$  atom bond strength is higher than the strength of the interatomic bonds constituting Ge-Sb-Te (most of them are covalent bonds) by the strength corresponding to the above-described ionic bond strength.

Therefore, when the  $I_2VI_6$  type stoichiometric compound is mixed with a multi-element stoichiometric compound composed of elements selected from at least two groups of the group  $III_b$  (i.e., Ga, In, and Tl), the group  $IV_b$  (i.e., Ge, Sn, and Pb), the group  $V_b$  (i.e., As, Sb, and Bi), and the  $VI_b$  (i.e., S, Se, and Te), the mixture contains a group I atom-group  $VI_b$  atom bond having high bond strength and thereby has a reduced free energy in the crystal phase thereof. As a result, a difference in free energy between the crystal phase and the amorphous phase, i.e., a transition energy, increases. This is assumed to be the reason why recording material (iii) has a reduced time of crystallization as compared with the conventional Ge-Sb-Te recording material.



The fact that the conventional  $\text{Sb}_2\text{Te}_3$  recording material has a short crystallization time, though it contains no bond exhibiting strong ionic bond strength, is not opposed to the consideration mentioned above because such a short crystallization time is believed to arise from its small activation energy but not from large transition energy.

On the other hand, the reason, the inventors believe, for the improved stability of recording material (iii) in its amorphous phase as compared with the conventional Ge-Sb-Te or  $\text{Sb}_2\text{Te}_3$  recording material is as follows.

As discussed above, Ge-Sb-Te has weak character of ionic bond and strong character of covalent bond. Therefore, according as the number of elements increases, the amorphous phase easily becomes unstable due to an increase of free energy with the increasing strain. To the contrary, since recording material (iii) has strong character of ionic bond which is less limited by bond direction or bond distance, it is stabilized in spite of a somewhat strained structure and thus exhibits higher stability in its amorphous phase than Ge-Sb-Te.

Further, since recording material (iii) is a multi-element material composed of three or more elements, the inhibitory effect on atomic movement due to differences in atomic radius is greater, and the activation energy is so greater than the two-element material  $\text{Sb}_2\text{Te}_3$ . The high stability of recording material (iii) in its amorphous phase would also be explained from this point of view.

#### 20 Recording Materials (iv) and (v):

The  $\text{III}_b\text{VI}_b$  type stoichiometric compound in recording material (iv) includes GaS, GaSe, GaTe, InS, InSe, InTe, TlS, TlSe, TlTe, GaInS<sub>2</sub>, GaInSe<sub>2</sub>, Ga<sub>2</sub>InSe<sub>3</sub>, Ga<sub>2</sub>SeTe, Ga<sub>3</sub>Se<sub>2</sub>Te, GaTlSe<sub>2</sub>, and InTlSe<sub>2</sub>.

The multi-element stoichiometric compound in recording material (iv) includes stoichiometric compounds composed of elements arbitrarily selected from at least two groups of the groups  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$ . Examples of such multi-element stoichiometric compounds are  $\text{IV}_b\text{VI}_b$  type stoichiometric compounds composed of the group  $\text{IV}_b$  element selected from Ge, Sn, and Pb and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{IV}_b\text{VI}_b$ ;  $\text{IV}_b\text{VI}_{b2}$  type stoichiometric compounds composed of the group  $\text{IV}_b$  element selected from Ge, Sn, and Pb and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{IV}_b\text{VI}_{b2}$ ; and  $\text{III}_b\text{VI}_b$  type stoichiometric compounds composed of the group  $\text{III}_b$  element selected from Ga, In, and Tl and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{III}_b\text{VI}_b$ .

Specific examples of the  $\text{IV}_b\text{VI}_b$  type stoichiometric compounds are GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, PbTe, GeSnTe<sub>2</sub>, and Ge<sub>2</sub>SeTe.

Specific examples of the  $\text{IV}_b\text{VI}_{b2}$  type stoichiometric compounds are GeS<sub>2</sub>, GeSe<sub>2</sub>, SnS<sub>2</sub>, SnSe<sub>2</sub>, and SnTe<sub>2</sub>.

Specific examples of the  $\text{III}_b\text{VI}_b$  type stoichiometric compounds are the same as above enumerated, i.e., GaS, GaSe, GaTe, InS, InSe, InTe, TlS, TlSe, TlTe, GaInS<sub>2</sub>, GaInSe<sub>2</sub>, Ga<sub>2</sub>InSe<sub>3</sub>, Ga<sub>2</sub>SeTe, Ga<sub>3</sub>Se<sub>2</sub>Te, GaTlSe<sub>2</sub>, and InTlSe<sub>2</sub>.

Recording material (iv) which has a composition corresponding to a mixture of the  $\text{III}_b\text{VI}_b$  type stoichiometric compound and the multi-element stoichiometric compound may be any of materials composed of at least three elements selected from the group  $\text{III}_b$  elements (i.e., Ga, In, and Tl), the  $\text{IV}_b$  elements (i.e., Ge, Sn and Pb), the group  $\text{V}_b$  elements (i.e., As, Sb, and Bi), and the group  $\text{VI}_b$  elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $\text{III}_b\text{VI}_b$  type stoichiometric compound with a multi-element stoichiometric compound (e.g., a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound, a  $\text{IV}_b\text{VI}_{b2}$  type stoichiometric compound, and a  $\text{III}_b\text{VI}_b$  type stoichiometric compound) at an arbitrary mixing ratio. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture, and the total content of Se and Te in the recording material is preferably not less than 30 atomic% based on the total atoms constituting the recording material. Examples of such a composition include a composition consisting of three elements containing Se and/or Te, a composition consisting of four elements containing Se and/or Te, and compositions consisting of more than four elements (e.g., a five-element composition and a six-element composition).

Specific examples of recording material (vi) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $\text{III}_b\text{VI}_b$  type stoichiometric compound with a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound selected from GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, PbTe, GeSnTe<sub>2</sub>, Ge<sub>2</sub>SeTe, etc. at an arbitrary ratio; stoichiometric compounds made of these mixtures, e.g., Ga<sub>2</sub>GeTe<sub>3</sub>, In<sub>2</sub>GeTe<sub>3</sub>, In<sub>3</sub>SnTe<sub>4</sub>, InPbTe<sub>2</sub>, TlGeTe<sub>2</sub>, and Tl<sub>2</sub>GeTe<sub>3</sub>; congruent compounds

made of these mixtures, e.g.,  $\text{GaGeTe}_2$  and  $\text{InGeTe}_2$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio.

Further included in recording material (iv) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $\text{III}_b\text{VI}_b$  type stoichiometric compound and a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound, e.g.,  $\text{GeS}_2$ ,  $\text{GeSe}_2$ ,  $\text{SnS}_2$ ,  $\text{SnSe}_2$ , and  $\text{SnTe}_2$ , at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $\text{GaGeSe}_3$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio.

Furthermore included in recording material (iv) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $\text{III}_b\text{VI}_b$  stoichiometric compound with a  $\text{III}_b\text{VI}_b$  type stoichiometric compound, e.g.,  $\text{GaS}$ ,  $\text{GaSe}$ ,  $\text{GaTe}$ ,  $\text{InS}$ ,  $\text{InSe}$ ,  $\text{InTe}$ ,  $\text{TlS}$ ,  $\text{TlSe}$ ,  $\text{TlTe}$ ,  $\text{GaInS}_2$ ,  $\text{GaInSe}_2$ ,  $\text{Ga}_2\text{InSe}_3$ ,  $\text{Ga}_2\text{SeTe}$ ,  $\text{Ga}_3\text{Se}_2\text{Te}$ ,  $\text{GaTlSe}_2$ , and  $\text{InTlSe}_2$ , at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $\text{GaInSe}_2$ ,  $\text{Ga}_2\text{InSe}_3$ , and  $\text{Ga}_3\text{SeTe}_2$ ; congruent compounds made of these mixtures, e.g.,  $\text{GaTlSe}_2$ ,  $\text{InTlSe}_2$ , and  $\text{Ga}_2\text{SeTe}$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary mixing ratio.

In recording material (v), the  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound includes those containing the same  $\text{III}_b$  elements and the same  $\text{VI}_b$  elements, e.g.,  $\text{Ga}_2\text{S}_3$ ,  $\text{Ga}_2\text{Se}_3$ ,  $\text{Ga}_2\text{Te}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{Se}_3$ ,  $\text{In}_2\text{Te}_3$ ,  $\text{Tl}_2\text{S}_3$ ,  $\text{Tl}_2\text{Se}_3$ , and  $\text{Tl}_2\text{Te}_3$ , and those containing different  $\text{III}_b$  elements or different  $\text{VI}_b$  elements, e.g.,  $\text{In}_2\text{STe}_2$ .

The multi-element stoichiometric compound in recording material (v) is a stoichiometric compound composed of elements selected from at least two groups of the groups  $\text{III}_b$ ,  $\text{IV}_b$ , and  $\text{VI}_b$ , including  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compounds composed of the group  $\text{III}_b$  element selected from Ga, In, and Tl and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{III}_{b2}\text{VI}_{b3}$ ; and  $\text{IV}_b\text{VI}_b$  type stoichiometric compounds composed of the group  $\text{IV}_b$  element selected from Ge, Sn, and Pb and the group  $\text{VI}_b$  element selected from S, Se, and Te and represented by chemical formula  $\text{IV}_b\text{VI}_b$ .

Specific examples of the  $\text{III}_{b2}\text{VI}_{b3}$  stoichiometric compounds are the same as enumerated above, i.e.,  $\text{Ga}_2\text{S}_3$ ,  $\text{Ga}_2\text{Se}_3$ ,  $\text{Ga}_2\text{Te}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{Se}_3$ ,  $\text{In}_2\text{Te}_3$ ,  $\text{Tl}_2\text{S}_3$ ,  $\text{Tl}_2\text{Se}_3$ , and  $\text{In}_2\text{STe}_2$ .

Specific examples of the  $\text{IV}_b\text{VI}_b$  type stoichiometric compounds are the same as enumerated above, i.e.,  $\text{GeS}$ ,  $\text{GeSe}$ ,  $\text{GeTe}$ ,  $\text{SnS}$ ,  $\text{SnSe}$ ,  $\text{SnTe}$ ,  $\text{PbS}$ ,  $\text{PbSe}$ ,  $\text{PbTe}$ ,  $\text{GeSnTe}_2$ , and  $\text{Ge}_2\text{SeTe}$ .

Recording material (v) which has a composition corresponding to a mixture of the above-described  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound and the multi-element stoichiometric compound may be any of materials composed of at least three elements selected from the group  $\text{III}_b$  elements (i.e., Ga, In, and Tl), the group  $\text{IV}_b$  elements (i.e., Ge, Sn and Pb), and the group  $\text{VI}_b$  elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound with a multi-element stoichiometric compound (e.g., a  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound and a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound) at an arbitrary mixing ratio. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture, and the total content of Se and Te in the recording material is preferably not less than 30 atomic% based on the total atoms constituting the recording material. Examples of such a composition include a composition consisting of three elements containing Se and/or Te, a composition consisting of four elements containing Se and/or Te, and compositions consisting of more than four elements (e.g., a five-element composition and a six-element composition).

Specific examples of recording material (v) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compounds, e.g.,  $\text{Ga}_2\text{S}_3$ ,  $\text{Ga}_2\text{Se}_3$ ,  $\text{Ga}_2\text{Te}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{Se}_3$ ,  $\text{In}_2\text{Te}_3$ ,  $\text{Tl}_2\text{S}_3$ ,  $\text{Tl}_2\text{Se}_3$ ,  $\text{Tl}_2\text{Te}_3$ , and  $\text{In}_2\text{STe}_2$ , at an arbitrary ratio; congruent compounds made of these mixtures, e.g.,  $\text{In}_2\text{STe}_2$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described congruent compounds, solid solutions, etc. at an arbitrary ratio.

Further included in recording material (v) are mixtures composed of at least three elements containing Se and/or Te which are obtained by mixing the above-described  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound and a  $\text{IV}_b\text{VI}_b$  type stoichiometric compound, e.g.,  $\text{GeS}$ ,  $\text{GeSe}$ ,  $\text{GeTe}$ ,  $\text{SnS}$ ,  $\text{SnSe}$ ,  $\text{SnTe}$ ,  $\text{PbS}$ ,  $\text{PbSe}$ ,  $\text{PbTe}$ ,  $\text{GeSnTe}_2$ , and  $\text{Ge}_2\text{SeTe}$ , at an arbitrary mixing ratio; stoichiometric compounds made of these mixtures, e.g.,  $\text{Ga}_4\text{SnTe}_7$ ; solid solutions made of these mixtures, which are composed of at least three elements containing Se and/or Te; and mixtures of the above-described stoichiometric compounds, solid solutions, etc. at an arbitrary ratio.

Use of recording material (iv) or (v) makes it possible to increase stability of the amorphous phase of the recording layer and to reduce the crystallization time of the recording layer.

The reason for the reduction of the crystallization time of the above-described recording material layer as compared with the conventionally employed Ge-Sb-Te recording material layer is believed to be the same as set forth above with respect to recording material (iii). More specifically, in the  $\text{III}_b\text{VI}_b$  type stoichiometric compounds constituting a part of recording material (iv) and the  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compounds constituting a part of recording material (v), a difference in electronegativity between Te whose electronegativity is the lowest (1.47) of the group  $\text{VI}_b$  elements and Ga whose electronegativity is the highest (1.13) of the group  $\text{III}_b$  elements is 0.34. On the other hand, a difference between S whose electronegativity is the highest (1.87) of the group  $\text{VI}_b$  elements and Tl whose electronegativity is the lowest (0.94) of the group  $\text{III}_b$  elements is 0.93. That is, the electronegativity difference between the group  $\text{III}_b$  elements and the group  $\text{VI}_b$  elements widely ranges from 0.34 to 0.93, indicating strong ionic bond strength between the group  $\text{III}_b$  atom and the group  $\text{VI}_b$  atom.

From these considerations, it is believed that the group  $\text{III}_b$  atom-group  $\text{VI}_b$  atom bond strength is higher than the strength of the interatomic bonds constituting Ge-Sb-Te (most of them are covalent bonds) by the strength corresponding to the ionic bond strength.

Therefore, when the  $\text{III}_b\text{VI}_b$  type stoichiometric compound is mixed with a multi-element stoichiometric compound composed of elements selected from at least two groups of the group  $\text{III}_b$  (i.e., Ga, In, and Tl), the group  $\text{IV}_b$  (i.e., Ge, Sn, and Pb), the group  $\text{V}_b$  (i.e., As, Sb, and Bi), and the  $\text{VI}_b$  (i.e., S, Se, and Te), or when the  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound is mixed with a multi-element stoichiometric compound composed of elements selected from at least two groups of the group  $\text{III}_b$  (i.e., Ga, In, and Tl), the group  $\text{IV}_b$  (i.e., Ge, Sn, and Pb), and the group  $\text{VI}_b$  (i.e., S, Se, and Te), the resulting mixture contains a group  $\text{III}_b$  atom-group  $\text{VI}_b$  atom having high bond strength. As a result, the mixture has reduced free energy in its crystal phase as compared with Ge-Sb-Te and thereby has a greater difference in free energy between the crystal phase and the amorphous phase, i.e., a greater transition energy. This seems to be the reason why recording materials (iv) and (v) have a reduced time of crystallization as compared with the conventional Ge-Sb-Te recording material.

It is considered that the higher stability of the amorphous phase of recording materials (iv) and (v) as compared with Ge-Sb-Te can also be accounted for by the reason stated above with respect to recording material (iii).

#### Recording Materials (vi-1) to (vi-9):

Recording materials (vi-1) to (vi-9) achieve further improvement in stability in the amorphous phase while having a rate of crystallization equal to that of the above-described recording materials (i) to (v).

In recording material (vi-1), the  $\text{IV}_b\text{VI}_b$  type stoichiometric compound includes SnS, SnSe, SnTe, PbS, PbSe, and PbTe, and the  $\text{V}_{b2}\text{VI}_{b3}$  type stoichiometric compound includes  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , and  $\text{As}_2\text{Te}_3$ .

The stoichiometric three-element compound having a composition corresponding to a mixture of the  $\text{IV}_b\text{VI}_b$  type stoichiometric compound and the  $\text{V}_{b2}\text{VI}_{b3}$  type stoichiometric compound may be any of stoichiometric three-element compounds consisting of three elements selected from the  $\text{IV}_b$  elements (i.e., Sn and Pb), the group  $\text{V}_b$  elements (i.e., Sb, Bi, and As), and the group  $\text{VI}_b$  elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition corresponding to a mixture of the  $\text{IV}_b\text{VI}_b$  type stoichiometric compound and the  $\text{V}_{b2}\text{VI}_{b3}$  type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Specific examples of such stoichiometric three-element compounds are  $\text{Sn}_2\text{Sb}_2\text{Se}_5$ ,  $\text{Sn}_2\text{Sb}_6\text{Se}_{11}$ ,  $\text{SnSb}_2\text{Te}_4$ ,  $\text{Pb}_2\text{Sb}_6\text{Te}_{11}$ ,  $\text{SnBi}_2\text{Te}_4$ ,  $\text{PbBi}_4\text{Se}_7$ ,  $\text{PbBi}_2\text{Se}_4$ ,  $\text{Pb}_3\text{Bi}_4\text{Se}_9$ , and  $\text{PbBi}_4\text{Te}_7$ .

In recording material (vi-1), at least one of the constituent elements of the above-described stoichiometric three-element compound is partly substituted by at least one of other elements selected from elements of the above-enumerated groups and Si and Ge belonging to the group  $\text{IV}_b$  (i.e., the group  $\text{IV}_b$  element selected from Sn, Pb, Si, and Ge, the group  $\text{V}_b$  element selected from Sb, Bi, and As, and the group  $\text{VI}_b$  element selected from S, Se and Te) to thereby form a solid solution containing 4 or more kinds of elements and containing at least one of Se and Te.

The upper limit of the degree of substitution of the three elements constituting the stoichiometric three-element compound is the degree where the composition containing 4 or more kinds of elements resulted from the substitution no longer constitutes a solid solution possessing the crystal structure of the stoichiometric three-element compound. As long as the degree of substitution is below such a limit, the constituent element(s) may be substituted by other element(s) to an arbitrary extent. Where one constituent element is partly substituted by one other element, there is produced a four-element solid solution; and

where it is partly substituted by two other elements, there is produced a five-element solid solution. Where each of two constituent elements is partly substituted by one other element, respectively, there is obtained a five-element solid solution. Where each of three constituent elements is partly substituted by one other element, respectively, there is obtained a six-element solid solution.

5 In the cases where the constituent element to be substituted and the other element substituting for the constituent element are in the relationship that they can form a solid solution regardless the mixing ratio of the former element to the latter element (hereafter, referred to as a "full-range solid solution"), the strain of crystal structure attended by the substitution is relatively small so that structural changes of the stoichiometric three-element compound due to the substitution can be minimized. Therefore, a permissible  
10 degree of substitution can be broadened to advantage. Examples of combinations of elements having such a relationship are a combination of Ge and Si (the group IV<sub>b</sub> elements), a combination of Sb and Bi (the group V<sub>b</sub> elements), and a combination of Se and Te (the group VI<sub>b</sub> elements).

The terminology "crystal structure of a stoichiometric three-element compound" as used herein means a structure of a certain stoichiometric three-element compound specified by atomic arrangement in a crystal  
15 lattice characteristic of the stoichiometric three-element compound. The terminology "solid solution possessing a crystal structure of a stoichiometric three-element compound" as used herein means a solid solution in which a part of atoms on lattice points of a crystal lattice characteristic of the stoichiometric three-element compound is substituted by a different atom(s) at random in such a manner that the different atom may be regarded as being uniformly dissolved in the crystal lattice.

20 Recording materials (vi-2) to (vi-4) correspond to improved recording material (iii).

In recording material (vi-2), the I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound includes Li<sub>2</sub>S, Li<sub>2</sub>Se, Li<sub>2</sub>Te, Na<sub>2</sub>S, Na<sub>2</sub>Se, Na<sub>2</sub>Te, K<sub>2</sub>S, K<sub>2</sub>Se, K<sub>2</sub>Te, Rb<sub>2</sub>S, Rb<sub>2</sub>Se, Rb<sub>2</sub>Te, Cs<sub>2</sub>S, Cs<sub>2</sub>Se, Cs<sub>2</sub>Te, Cu<sub>2</sub>S, Cu<sub>2</sub>Se, Cu<sub>2</sub>Te, Ag<sub>2</sub>S, Ag<sub>2</sub>Se, Ag<sub>2</sub>Te, Au<sub>2</sub>S, Au<sub>2</sub>Se, and Au<sub>2</sub>Te. The V<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound includes Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub>, and As<sub>2</sub>Te<sub>3</sub>.

25 The stoichiometric three-element compound which has a composition corresponding to a mixture of the I<sub>b</sub>VI<sub>b</sub> type stoichiometric compound and the V<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound may be any of stoichiometric three-element compounds consisting of three elements selected from the group I elements (i.e., Li, Na, K, Rb, Cs, Cu, Ag, and Au), the group V<sub>b</sub> elements (i.e., As, Sb, and Bi), and the group VI<sub>b</sub> elements (i.e., S, Se, and Te), containing at least one of Se and Te, and having a composition  
30 corresponding to a mixture obtained by mixing the I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound with the V<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds are Sn<sub>2</sub>Sb<sub>2</sub>Se<sub>5</sub>, Sn<sub>2</sub>Sb<sub>5</sub>Se<sub>11</sub>, SnSb<sub>2</sub>Te<sub>4</sub>, Pb<sub>2</sub>Sb<sub>5</sub>Te<sub>11</sub>, SnBi<sub>2</sub>Te<sub>4</sub>, PbBi<sub>4</sub>Se<sub>7</sub>, PbBi<sub>2</sub>Se<sub>4</sub>, Pb<sub>3</sub>Bi<sub>4</sub>Se<sub>9</sub>, and PbBi<sub>4</sub>Te<sub>7</sub>.

35 Recording material (vi-2) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from elements of the above-enumerated groups, i.e., the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au, the group V<sub>b</sub> element selected from As, Sb, and Bi, and the group VI<sub>b</sub> element selected from S, Se, and Te.

40 In recording material (vi-3), the I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound is the same as in recording material (vi-2), and the III<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound includes Ga<sub>2</sub>S<sub>3</sub>, Ga<sub>2</sub>Se<sub>3</sub>, Ga<sub>2</sub>Te<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, In<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>Te<sub>3</sub>, Tl<sub>2</sub>S<sub>3</sub>, Tl<sub>2</sub>Se<sub>3</sub>, and Tl<sub>2</sub>Te<sub>3</sub>.

The stoichiometric three-element compound which has a composition corresponding to a mixture of the I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound and the III<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound may be any of  
45 stoichiometric compounds consisting of three elements selected from the group I elements including Li, Na, K, Rb, Cs, Cu, Ag, and Au, the group III<sub>b</sub> elements including Ga, In, and Tl, and the group VI<sub>b</sub> elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound with the III<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from  
50 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds are CuGaSe<sub>2</sub>, CuInSe<sub>2</sub>, CuInTe<sub>2</sub>, AgInTe<sub>2</sub>, AgGaSe<sub>2</sub>, and AgIn<sub>2</sub>Se<sub>3</sub>.

Recording material (vi-3) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from elements of the  
55 above-enumerated groups and At belonging to the group III<sub>b</sub>, i.e., the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au, the group III<sub>b</sub> element selected from Al, Ga, In, and Tl, and the group VI<sub>b</sub> element selected from S, Se, and Te.

To assure an increased rate of crystallization, it is advantageous that the "other element" which

substitutes for a part of the constituent elements of the stoichiometric three-element compound is Tl.

In recording material (vi-4), examples of the  $I_2VI_6$  type stoichiometric compound are the same as those mentioned for recording material (vi-2). Examples of the  $IV_6VI_{12}$  type stoichiometric compound are  $GeSe_2$ ,  $GeSe_2$ ,  $SnS_2$ , and  $SnSe_2$ .

- 5 The stoichiometric three-element compound which has a composition corresponding to a mixture of the  $I_2VI_6$  type stoichiometric compound and the  $IV_6VI_{12}$  type stoichiometric compound may be any of stoichiometric compounds consisting of three elements selected from the group I elements including Li, Na, K, Rb, Cs, Cu, Ag, and Au, the group  $IV_6$  elements including Ge, Sn, and Pb, and the group  $VI_6$  elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $I_2VI_6$  type stoichiometric compound with the  $IV_6VI_{12}$  type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds include  $Cu_2SnSe_3$ .

- 15 Recording material (vi-4) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from the group consisting of elements of the above-enumerated groups and Si belonging to the group  $IV_6$ , i.e., the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au, the group  $IV_6$  element selected from Si, Ge, Sn, and Pb, and the group  $VI_6$  element selected from S, Se, and Te.

- 20 Recording materials (vi-5), (vi-6), and (vi-7) correspond to improved recording material (iv).

In recording material (vi-5), the  $III_6VI_6$  type stoichiometric compound includes GaS, GaSe, GaTe, InS, InSe, InTe, TlS, TlSe, and TlTe. The  $IV_6VI_6$  type stoichiometric compound includes GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, and PbTe.

- 25 The stoichiometric three-element compound which has a composition corresponding to a mixture of the  $III_6VI_6$  type stoichiometric compound and the  $IV_6VI_6$  type stoichiometric compound may be any of stoichiometric compounds consisting of three elements selected from the group  $III_6$  elements including Ga, In, and Tl, the group  $IV_6$  elements including Ge, Sn, and Pb, and the group  $VI_6$  elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $III_6VI_6$  type stoichiometric compound with the  $IV_6VI_6$  type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds are  $Ga_2GeTe_3$ ,  $GaGeTe_2$ ,  $In_2GeTe_3$ ,  $In_3SnTe_4$ ,  $InPbTe_2$ ,  $InGeTe_2$ ,  $TlGeTe_2$ , and  $Tl_2GeTe_3$ .

- 30 Recording material (vi-5) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from the group consisting of the above-enumerated elements, Al belonging to the group  $III_6$ , and Si belonging to the group  $IV_6$ , i.e., the group  $III_6$  element selected from Al, Ga, In, and Tl, the group  $IV_6$  element selected from Si, Ge, Sn, and Pb, and the group  $VI_6$  element selected from S, Se, and Te.

- 40 In recording material (vi-6), examples of the  $III_6VI_6$  type stoichiometric compound are the same as those enumerated with respect to recording material (vi-5), and examples of the  $IV_6VI_{12}$  type stoichiometric compound are  $GeSe_2$ ,  $GeSe_2$ ,  $SnS_2$ ,  $SnSe_2$ , and  $SnTe_2$ .

- The stoichiometric three-element compound which has a composition corresponding to a mixture of the  $III_6VI_6$  type stoichiometric compound and the  $IV_6VI_{12}$  type stoichiometric compound may be any of stoichiometric compounds consisting of three elements selected from the group  $III_6$  elements including Ga, In, and Tl, the group  $IV_6$  elements including Ge, Sn, and Pb, and the group  $VI_6$  elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the  $III_6VI_6$  type stoichiometric compound with the  $IV_6VI_{12}$  type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds are  $GaGeSe_3$ .

- 50 Recording material (vi-6) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from the group consisting of the above-enumerated elements, Al belonging to the group  $III_6$ , and Si belonging to the group  $IV_6$ , i.e., the group  $III_6$  element selected from Al, Ga, In, and Tl, the group  $IV_6$  element selected from Si, Ge, Sn, and Pb, and the group  $VI_6$  element selected from S, Se, and Te.

In recording material (vi-7), examples of the  $III_6VI_6$  type stoichiometric compound are the same as those enumerated with respect to recording material (vi-5).

The stoichiometric three-element compound which has a composition corresponding to a mixture of two

III<sub>6</sub>VI<sub>6</sub> type stoichiometric compounds may be any of stoichiometric compounds consisting of three elements selected from the group III<sub>6</sub> elements including Ga, In, and Tl and the group VI<sub>6</sub> elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing two III<sub>6</sub>VI<sub>6</sub> type stoichiometric compounds. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds are GaInSe<sub>2</sub>, Ga<sub>2</sub>InSe<sub>3</sub>, Ga<sub>3</sub>SeTe<sub>2</sub>, Ga<sub>2</sub>SeTe, GaTlSe<sub>2</sub>, and InTlSe<sub>2</sub>.

Recording material (vi-7) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from the group consisting of the above-enumerated elements and Al belonging to the group III<sub>6</sub>, i.e., the group III<sub>6</sub> element selected from Al, Ga, In, and Tl and the group VI<sub>6</sub> element selected from S, Se, and Te.

Recording materials (vi-8), (vi-7), and (vi-9) correspond to improved recording material (v).

In recording material (vi-8), the III<sub>62</sub>VI<sub>63</sub> type stoichiometric compound includes Ga<sub>2</sub>S<sub>3</sub>, Ga<sub>2</sub>Se<sub>3</sub>, Ga<sub>2</sub>Te<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, In<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>Te<sub>3</sub>, Tl<sub>2</sub>S<sub>3</sub>, Tl<sub>2</sub>Se<sub>3</sub>, and Tl<sub>2</sub>Te<sub>3</sub>.

The stoichiometric three-element compound which has a composition corresponding to a mixture of two III<sub>62</sub>VI<sub>63</sub> type stoichiometric compounds may be any of stoichiometric compounds consisting of three elements selected from the group III<sub>6</sub> elements including Ga, In, and Tl, and the group VI<sub>6</sub> elements including S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing two III<sub>62</sub>VI<sub>63</sub> type stoichiometric compounds. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds include In<sub>2</sub>STe<sub>2</sub>.

Recording material (vi-8) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric three-element compound by at least one of other elements selected from the group consisting of the above-enumerated elements and Al belonging to the group III<sub>6</sub>, i.e., the group III<sub>6</sub> element selected from Al, Ga, In, and Tl and the group VI<sub>6</sub> element selected from S, Se, and Te.

In recording material (vi-9), examples of the III<sub>62</sub>VI<sub>63</sub> type stoichiometric compound are the same as those enumerated with respect to recording material (vi-8), and examples of the IV<sub>6</sub>VI<sub>6</sub> type stoichiometric compound are GeS, SeSe, SeTe, SnS, SnSe, SnTe, PbS, PbSe, and PbTe.

The stoichiometric three-element compound which has a composition corresponding to a mixture of the III<sub>62</sub>VI<sub>63</sub> type stoichiometric compound and the IV<sub>6</sub>VI<sub>6</sub> type stoichiometric compound may be any of stoichiometric compounds consisting of three elements selected from the group III<sub>6</sub> element selected from Ga, In, and Tl, the group IV<sub>6</sub> element selected from Ge, Sn, and Pb, and the group VI<sub>6</sub> element selected from S, Se, and Te, containing at least one of Se and Te, and having a composition corresponding to a mixture obtained by mixing the III<sub>62</sub>VI<sub>63</sub> type stoichiometric compound with the IV<sub>6</sub>VI<sub>6</sub> type stoichiometric compound. The mixture preferably contains one of the two stoichiometric compounds in an amount of from 5 to 95 mol% based on the mixture. Examples of such stoichiometric three-element compounds include GaSnTe<sub>7</sub>.

Recording material (vi-9) is characterized by comprising a solid solution containing 4 or more kinds of elements, obtained by partly substituting at least one of the constituent elements of the above-described stoichiometric ternary compound by at least one of other elements selected from the group consisting of the above-enumerated elements, Al belonging to the group III<sub>6</sub>, and Si belonging to the group IV<sub>6</sub>, i.e., the group III<sub>6</sub> element selected from Al, Ga, In, and Tl, the group IV<sub>6</sub> element selected from Si, Ge, Sn, and Pb, and the group VI<sub>6</sub> element selected from S, Se, and Te.

In recording materials (vi-2) to (vi-9), the upper limit of the degree of substitution of the three elements constituting the stoichiometric three-element compound is the degree where the composition containing 4 or more kinds of elements resulted from the substitution no longer constitutes a solid solution possessing the crystal structure of the stoichiometric three-element compound. As long as the degree of substitution is below such a limit the constituent element(s) may be substituted by other element(s) to an arbitrary extent.

In the cases where the constituent element to be substituted and the other element substituting for the constituent element those capable of forming a full-range solid solution, the strain of crystal structure attended by the substitution is relatively small so that structural changes of the stoichiometric three-element compound due to the substitution can be minimized. Therefore, a permissible degree of substitution can be broadened to advantage similarly to the case of recording material (vi-1).

To assure an increased rate of crystallization, it is advantageous to use Tl as the "other element" which substitutes for a part of the constituent elements of the stoichiometric three-element compound, similarly to the case of recording material (vi-3).



In recording materials (vi-1) to (vi-9), the degree of substitution of the three elements constituting the stoichiometric three-element compounds is preferably not less than 0.5% of the element(s) a part of which is or are substituted, and the total content of Se and Te in recording material is preferably not less than 30 atomic% based on the total atoms constituting the recording material.

As mentioned above, since the recording material layer using each of recording materials (vi-1) to (vi-9) has a crystal structure of a stoichiometric three-element compound, it has an increased rate of crystallization and exhibits improved stability in its amorphous phase. Further, being comprised of a solid solution in which at least one of the three elements constituting the stoichiometric three-element compound is partly substituted with other element(s), the recording layer exhibits further enhanced stability in the amorphous phase.

The increased rate of crystallization obtained by using recording material (vi-1) seems to be based on the same reason as described with respect to recording material (i) or (ii); and that obtained by using recording materials (vi-2) to (vi-9) is believed to be based on the same reason as described with respect to recording material (iii).

More specifically, in the  $I_2VI_b$  type stoichiometric compounds constituting a part of recording materials (vi-2) to (vi-4), a difference in electronegativity between Te whose electronegativity is the lowest (1.47) of the group  $VI_b$  elements and Li whose electronegativity is the highest (1.00) of the group I elements is 0.47. On the other hand, a difference between S whose electronegativity is the highest (1.87) of the group  $VI_b$  elements and Ag whose electronegativity is the lowest (0.57) of the group I elements is 1.30. That is, the electronegativity difference between the group I element and the group  $VI_b$  element widely ranges from 0.47 to 1.30, indicating high ionic bond strength between the group I atom and the group  $VI_b$  atom.

Likewise, in the  $III_bVI_b$  type stoichiometric compounds constituting a part of recording materials (vi-5) to (vi-9), a difference in electronegativity between Te whose electronegativity is the lowest (1.47) of the group  $VI_b$  elements and Ga whose electronegativity is the highest (1.13) of the group  $III_b$  elements is 0.34. On the other hand, a difference between S whose electronegativity is the highest (1.87) of the group  $VI_b$  elements and Tl whose electronegativity is the lowest (0.94) of the group  $III_b$  elements is 0.93. That is, the electronegativity difference between the group  $III_b$  element and the group  $VI_b$  element widely ranges from 0.34 to 0.93, indicating high ionic bond strength between the group  $III_b$  atom and the group  $VI_b$  atom.

From these considerations, it is believed that the group I atom-group  $VI_b$  atom bond strength or the group  $III_b$  atom-group  $VI_b$  atom bond strength is higher than the strength of the interatomic bonds constituting Ge-Sb-Te (most of them are covalent bonds) by the strength corresponding to the ionic bond strength.

In recording materials (vi-2) to (vi-4), the stoichiometric three-element compound having a composition corresponding to a mixture of the  $I_2VI_b$  type stoichiometric compound and the  $V_{b2}VI_{b3}$  type stoichiometric compound, the  $III_{b2}VI_{b3}$  type stoichiometric compound, or the  $IV_bVI_{b2}$  type stoichiometric compound contains a bond of the group I atom and the group  $VI_b$  atom exhibiting high bond strength. In recording materials (vi-5) to (vi-7), the stoichiometric compound having a composition corresponding to a mixture of the  $III_bVI_b$  type stoichiometric compound and the  $IV_bVI_b$  type stoichiometric compound, the  $IV_bVI_{b2}$  type stoichiometric compound, or the  $III_bVI_b$  type stoichiometric compound contains a bond of the group  $III_b$  atom and the group  $VI_b$  atom exhibiting high bond strength. In recording materials (vi-8) and (vi-9), the stoichiometric compound having a composition corresponding to a mixture of the  $III_{b2}VI_{b3}$  type stoichiometric compound and the  $III_{b2}VI_{b3}$  type stoichiometric compound or the  $IV_bVI_b$  type stoichiometric compound contains a bond of the group  $III_b$  atom and the group  $VI_b$  atom exhibiting high bond strength. As a result, these materials have a reduced free energy in the crystal phase thereof as compared with Ge-Sb-Te and thereby have a greater difference in free energy between the crystal phase and the amorphous phase, i.e., a greater transition energy. This is assumed to be the reason why recording materials (vi-2) to (vi-9) have an increased rate of crystallization as compared with the conventional Ge-Sb-Te recording material.

Further, it is considered that the higher stability of the amorphous phase of recording materials (vi-1) to (vi-9) as compared with the conventional Ge-Sb-Te or  $Sb_2Te_3$  recording materials can also be accounted for by the reason stated above with respect to recording material (iii).

In addition, recording materials (vi-1) to (vi-9) exert stronger inhibitory effects on atomic movement due to a difference in atomic radius from the nature of materials containing 4 or more kinds of elements and thus have higher activation energy as compared with the two-element material,  $Sb_2Te_3$ , or the three-element material, Ge-Sb-Te. From this viewpoint, too, these materials show further improved stability in the amorphous phase thereof.

Recording Material (vii):

Recording material (vii) is characterized by comprising a solid solution synthesized from plural elements or stoichiometric compounds having the same crystal system.

5 The term "crystal system" as used herein is in accordance with a classification of unit space lattices based on angle between two axes and length of axes, including seven crystal systems, i.e., triclinic, cubic, tetragonal, rhombohedral, orthorhombic, hexagonal, and monoclinic systems.

For example, Ga, In and Tl as the group III<sub>b</sub> elements; Ge, Sn, and Pb as the group IV<sub>b</sub> elements; As, Sb, and Bi as the group V<sub>b</sub> elements; S, Se, and Te as the group VI<sub>b</sub> elements; and stoichiometric  
10 compounds composed of these elements which constitute the solid solution of recording material (vii) can be classified based on the crystal system as shown in Table 3 below.

While a classification by strukturbericht, which relates to crystal structures taking the bond state of compounds into consideration in addition to the above-described classification of crystal system, divides crystals into A type (element) of from A1 to A20, B type (compound XY) of from B1 to b37, C type  
15 (compound XY<sub>2</sub>) of from C1 to C54, D type (X<sub>m</sub>Y<sub>n</sub>) of from D 0<sub>2</sub> to D 8<sub>11</sub>, H 1<sub>1</sub>, L 1<sub>0</sub> to L 2<sub>2</sub>, etc., it is preferred that the solid solution be synthesized from plural elements or stoichiometric compounds having the same crystal system based on the classification by strukturbericht. In Table 3, symbols in parentheses indicate crystal structure according to the classification by strukturbericht.

20

25

30

35

40

45

50

55



TABLE 3

	Rhombohedral		Orthorhombic	Cubic		Hexagonal	Tetragonal	Monoclinic
One-Element	As(A7) Bi(A7) Sb(A7)		Ga(A11) S(A17)	Pb(A1) Ti(A3) Ge(A4) Sn(A4)		S(A3) Ti(A3) Se(A8) Te(A8)	Sn(A5) In(A6)	S
Two-Element	Sb <sub>2</sub> Te <sub>3</sub> (C33) Bi <sub>2</sub> Te <sub>3</sub> (C33) Bi <sub>2</sub> Se <sub>3</sub> (C33) Sn <sub>4</sub> As <sub>3</sub> In <sub>2</sub> Se <sub>3</sub> Sn <sub>2</sub> As <sub>2</sub>		SnSe(B29) GeSe(B29) Sb <sub>2</sub> S <sub>3</sub> (D58) Bi <sub>2</sub> S <sub>3</sub> (D58) Sb <sub>2</sub> Se <sub>3</sub> (D58) In <sub>2</sub> Se In <sub>9</sub> Se <sub>7</sub> GeSe <sub>2</sub> SnS GeAs <sub>2</sub> InS Sn <sub>2</sub> S <sub>3</sub>	SnTe(B1) PbSe(B1) PbTe(B1) GeTe(B1) BiTe(B1) BiSe(B1) SnAs(B1) PbS(B1) Ti <sub>7</sub> Sb <sub>2</sub> (B2)	GaTe(B3) GaSb(B3) AsGa(B3) InAs(B3) InSb(B3) Ga <sub>2</sub> Se <sub>3</sub> (B3) Ga <sub>2</sub> Te <sub>3</sub> (B3)	GaSe InSe In <sub>2</sub> Bi(C32) TiBi <sub>2</sub> (C32) SnSe <sub>2</sub> GaTe <sub>3</sub> GaS	TiTe TiSe (B37) InTe (B37) InBi (B10) Ti <sub>2</sub> Se	GaTe GeAs Ti <sub>2</sub> Te <sub>3</sub> Ti <sub>2</sub> Se <sub>3</sub> In <sub>2</sub> Te <sub>5</sub> As <sub>2</sub> Te <sub>3</sub> Ga <sub>2</sub> S <sub>3</sub> In <sub>4</sub> S <sub>5</sub>
Three-Element	GeSb <sub>4</sub> Te <sub>7</sub> GeBi <sub>4</sub> Te <sub>7</sub> PbBi <sub>4</sub> Te <sub>7</sub> PbBi <sub>4</sub> Se <sub>7</sub> GeSb <sub>2</sub> Te <sub>4</sub> GeBi <sub>2</sub> Te <sub>4</sub> Bi <sub>2</sub> Te <sub>2</sub> S(C33)	SnSb <sub>2</sub> Te <sub>4</sub> SnBi <sub>2</sub> Te <sub>4</sub> PbBi <sub>2</sub> Se <sub>4</sub> Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub> Ge <sub>2</sub> Bi <sub>2</sub> Te <sub>5</sub> Sn <sub>2</sub> Sb <sub>2</sub> Se <sub>5</sub>	PbSnS <sub>2</sub>			GaGeTe <sub>2</sub> Ga <sub>2</sub> GeTe <sub>3</sub>		

The solid solution synthesized from plural elements or stoichiometric compounds having the same crystal system includes a solid solution containing three or more kinds of elements and containing Se and/or Te, which is synthesized by mixing at least three elements having the same crystal system; a solid solution containing three or more kinds of elements and containing Se and/or Te, which is synthesized by mixing at least one element and at least one two-element compound having the same crystal system; a solid solution containing three or more kinds of elements and containing Se and/or Te, which is synthesized by mixing at least one element and at least one three-element compound having the same crystal system; a solid solution containing three or more kinds of elements and containing Se and/or Te, which is synthesized by mixing at least two two-element compounds having the same crystal system; a solid solution containing three or more kinds of elements and containing Se and/or Te, which is obtained by mixing at least two three-element compounds having the same crystal system; and a solid solution containing three or more kinds of elements and containing Se and/or Te, which is synthesized by mixing a two-element compound and a three-element compound having the same crystal system.

Referring to Table 3 above, specific examples of these solid solutions include a solid solution containing three or more kinds of elements synthesized by mixing elements selected from Tl, S, Se, and Te, all of which belong to the hexagonal system; a solid solution containing three or more kinds of elements synthesized by mixing at least two 2-element compounds selected from  $\text{Sb}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Se}_3$ , etc., all of which belong to the rhombohedral system; a three-element solid solution synthesized by mixing SnTe (B1), GeTe (B1), and PbTe (B1), all of which belong to the cubic system; a three-element solid solution synthesized by mixing GeTe (B1), InSb (B3), and  $\text{Tl}_7\text{Sb}_2$  (B2), all of which belong to the cubic system; a solid solution containing three or more kinds of elements synthesized by mixing at least two three-element compounds selected from  $\text{GeSb}_2\text{Te}_4$ ,  $\text{Ge}_2\text{Bi}_2\text{Te}_5$ ,  $\text{PbBi}_4\text{Se}_7$ , etc., all of which belong to the rhombohedral system; a three-element solid solution synthesized by mixing an element, e.g., As, Bi, and Sb, and a two-element compound, e.g.,  $\text{Sb}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_3$ , all of which belong to the rhombohedral system; and a solid solution containing three or more kinds of elements synthesized by mixing a two-element compound, e.g.,  $\text{Sb}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_3$ , and a three-element compound, e.g.,  $\text{GeSb}_4\text{Te}_7$  and  $\text{GeBi}_2\text{Te}_4$ , all of which belong to the rhombohedral system.

The terminology "solid solution" as used herein means a phase which is formed by substituting an atom at a lattice point of a crystal phase characteristic of a certain element or compound by a different atom at random or a phase in which a different atom is statistically distributed in interstices of the lattice of a crystal phase characteristic of a certain element or compound, that is, a phase in which a foreign substance is uniformly dissolved in a certain crystal phase.

Of these solid solutions, congruent solid solution which has an inherent melting point and does not decompose up to this melting point are preferably used for recording material (vii).

Use of recording material (vii) makes it possible to shorten the time of crystallization of a recording material layer and, at the same time, to obtain increased stability in its amorphous phase.

The reason, the inventors believe, for the reduction in crystallization time achieved by recording material (vii) is as follows.

Recording material (vii) is comprised of a solid solution whose crystal phase is a single phase. Moreover, since the solid solution is synthesized from plural elements or stoichiometric compounds having the same crystal system, it has satisfactory crystal alignment with small lattice strain and a very small free energy in its crystal phase. Accordingly, the difference in free energy between the crystal phase and the amorphous phase, i.e., the transition energy becomes great to thereby reduce the time of crystallization in the recording material layer.

To the contrary, since the conventional Ge-Sb-Te recording material is synthesized by mixing cubic GeTe and rhombohedral  $\text{Sb}_2\text{Te}_3$ , it has extremely poor crystal alignment and contains large strain in the crystal lattice. Accordingly, the free energy in the crystal phase is large, and the difference in free energy between the crystal phase and the amorphous phase, i.e., the transition energy, is small. This appears to account for the slow crystallization of the conventional Ge-Sb-Te recording material layer.

The inventors believed, on the other hand, that the improvement in amorphous phase stability of recording material (vii) over the conventional  $\text{Sb}_2\text{Te}_3$  recording material arises from strong covalent bond character of interatomic bonds between constituent elements of recording material (vii), i.e., the group III<sub>b</sub> elements (Ga, In, and Tl), the group IV<sub>b</sub> elements (Ge, Sn, and Pb), the group V<sub>b</sub> elements (As, Sb, and Bi), and the group VI<sub>b</sub> elements (S, Se, and Te). Further, from the nature of a material containing three or more kinds of elements, recording material (vii) exerts strong inhibitory effects on atomic movement due to a difference of atomic radius thereby having larger activation energy than the two-element material,  $\text{Sb}_2\text{Te}_3$ . This is also a reason for the high stability of the amorphous phase.

In addition, since recording materials (i) to (vii) according to the present invention contain at least one of Se and Te, they absorb visible light and near infrared light.

The optical recording medium using the recording material according to the present invention basically comprises a light-transmitting substrate having thereon a recording material layer generally having a thickness of from 10 to 200 nm and preferably from 20 to 40 nm. For the purpose of preventing deformation of the recording material layer from being deformed in the period of from protecting the recording material layer from mechanical damage or oxidation, a protective layer may be provided on the recording material layer.

Examples of suitable light-transmitting substrates include glass and resin materials, e.g., acrylic resins, polycarbonate resins, and epoxy resins. In using resin materials, an inorganic dielectric material layer comprised of, for example,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnS}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{AlN}$ ,  $\text{Al}_2\text{O}_3$ , etc., or a mixture thereof, may be provided between the recording material layer and the substrate in order to prevent thermal damage of the resin material. The thickness of the inorganic dielectric material layer is generally from 50 to 200 nm. In optical recording media which perform recording, reproduction, and erasing by irradiation with a light beam from the side opposite to the substrate, the substrate may be, as a matter of course, comprised of a light non-transmitting material, such as aluminum.

Materials of the protective layer includes the same materials constituting the above-described inorganic dielectric material layer and, in addition, resin materials, e.g., ultraviolet curing resins, acrylic resins, polycarbonate resins, and epoxy resins, and glass. The protective layer may have either a single-layered structure or a multi-layered structure. The thickness of the protective layer is generally from 10 to 200 nm. Where a part of the protective layer in contact with the recording material layer is made of a resin material, an inorganic dielectric material layer may be inserted therebetween as in the case of the resinous substrate. Further, an adhesive layer of 1 to 10  $\mu\text{m}$  in thickness may also be provided between the protective layer and the inorganic dielectric material layer. For the purpose, conventional adhesives such as a ultraviolet curing adhesive may be used.

The recording material layer can be formed by sputtering, vacuum deposition, or the like technique. Sputtering can be carried out by simultaneous sputtering in which a plurality of targets are employed, and a controlled voltage is applied to each target to synthesize any desired composition and, at the same time, to deposit the composition onto a substrate. Sputtering can also be performed by using a single alloy target corresponding to the desired composition.

For example, a plurality of targets which can be used for forming a recording layer of recording material (i) or (ii) by simultaneous sputtering include alloy targets composed of the above-described  $\text{IV}_b\text{VI}_b$  type stoichiometric compound or  $\text{V}_{b2}\text{VI}_{b3}$  type stoichiometric compound, alloy targets prepared by arbitrarily mixing elements of the  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$  groups, and a single target made up of an element selected from the groups  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$ .

A plurality of targets which can be used for forming a recording layer of recording material (iii) by simultaneous sputtering include alloy targets composed of the above-described  $\text{I}_2\text{VI}_b$  type stoichiometric compound,  $\text{V}_{b2}\text{VI}_{b3}$  type stoichiometric compound,  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound, etc., alloy targets prepared by arbitrarily mixing elements of the I,  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$  groups, and a single target made up of an element selected from the groups I,  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$ .

A plurality of targets for forming a recording layer of recording material (iv) or (v) by simultaneous sputtering include alloy targets composed of the above-described  $\text{III}_b\text{VI}_b$  type stoichiometric compound,  $\text{IV}_b\text{VI}_b$  type stoichiometric compound,  $\text{IV}_b\text{VI}_{b2}$  type stoichiometric compound,  $\text{III}_{b2}\text{VI}_{b3}$  type stoichiometric compound, etc., alloy targets prepared by arbitrarily mixing elements of the  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$  groups, and a single target made up of an element selected from the groups  $\text{III}_b$ ,  $\text{IV}_b$ ,  $\text{V}_b$ , and  $\text{VI}_b$ .

The above-described vacuum deposition can be conducted by using a plurality of vapor sources and controlling the respective rate of vaporization to obtain a desired composition and simultaneously deposit the composition onto a substrate.

In the optical recording medium of the invention, the amorphous phase of the recording material layer may correspond to a recorded state, with the crystal phase to an erased state, or vice versa.

The present invention is now illustrated in greater detail by way of Examples and Comparative Examples, but it should be understood that the present invention is not deemed to be limited thereto.

In Examples and Comparative Examples, recording and erasing characteristics of optical recording media were evaluated in terms of time of crystallization and stability of amorphous phase according to the following standards.

#### Standards for Evaluation:

1. Time of Crystallization
  - Good ... Crystallization completes in 100 ns.
  - Poor ... Crystallization does not complete in 100 ns.
2. Stability
  - Good ... Crystallization temperature is 120 °C or higher.
  - Poor ... Crystallization temperature is less than 120 °C.

#### EXAMPLE 1 AND COMPARATIVE EXAMPLE 1

10

Optical recording media having a structure shown in Fig. 1 were prepared, each comprising 1.2 mm-thick acrylic resin substrate (1) having thereon 100 nm-thick inorganic dielectric material layer (2) made of SiO<sub>2</sub>, 100 nm-thick recording material layer (3) made of Sn-Sb-Te, 100 nm thick inorganic dielectric material layer (4) made of SiO<sub>2</sub>, ultraviolet curable acrylic resin adhesive layer (5), and 1.2 mm-thick acrylic resin protective layer (6) in this order.

Recording material layer (3) was formed by sputtering using a radio frequency (RF) magnetron and two alloy targets, SnTe and Sb<sub>2</sub>Te<sub>3</sub>. In more detail, the alloy targets were mounted in the RF magnetron sputtering chamber, and the pressure in the chamber was reduced to  $2 \times 10^{-6}$  Torr, followed by introducing argon gas to adjust the pressure to  $4 \times 10^{-3}$  Torr. The RF power applied to the respective alloy targets was suitably controlled within the range of from 25 to 200 W to obtain recording material layers having compositions shown in Table 4 below. The resulting optical recording media were designated Samples 1 to 3.

Comparative Samples 4 or 5 was prepared by using Sb-Te or Ge-Sb-Te, respectively, as a recording material, with the layer structure being the same as Samples 1 to 3. (Comparative Example 1) The recording material layer of Samples 4 or 5 was formed by RF magnetron sputtering using a single alloy target of Sb<sub>2</sub>Te<sub>3</sub> or two alloy targets of Sb<sub>2</sub>Te<sub>3</sub> and GeTe, respectively.

Samples 1 to 5 showed absorption in the wavelength region of from visible light to near infrared light and could be used as optical recording media at least in the wavelength region of from 400 nm to 860 nm.

Recording and erasure were carried out on each of Samples 1 to 5 using a semi-conductor laser having a wavelength of 830 nm as a light source. Recording and erasure characteristics were examined and evaluated according to the above-described standards, and the results obtained are shown in Table 4.

TABLE 4

35

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 1	1	(SnTe) <sub>40</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub>	good	good
"	2	(SnTe) <sub>50</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>50</sub>	good	good
"	3	(SnTe) <sub>60</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>40</sub>	good	good
Comparative Example 1	4	Sb <sub>2</sub> Te <sub>3</sub>	good	poor
"	5	(GeTe) <sub>67</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>33</sub>	poor	good

40

45

As is apparent from Table 4, Samples 1 to 3 according to the present invention have a reduced time of crystallization as compared with Sample 5 of Comparative Example 1, making it possible to conduct recording and erasure of information at a higher speed than in the conventional optical recording media, and have an increased crystallization temperature, an indication of improved stability of the amorphous phase, over Sample 4 of Comparative Example 1.

50

In particular, it was confirmed that the crystal phase in Sn-Sb-Te of Sample 2 is composed of a single phase of a congruent compound expected from the pseudo-binary phase diagram shown in Fig. 2, i.e., SnSb<sub>2</sub>Te<sub>4</sub> (shown as SnTe.Sb<sub>2</sub>Te<sub>3</sub> in the figure). This sample had a short crystallization time and exhibited satisfactory stability on repetition of rewriting.

55

Further, Sn-Sb-Te in Sample 1 had a composition corresponding to a mixture of SnSb<sub>2</sub>Te<sub>4</sub> which is a congruent compound and Sb<sub>2</sub>Te<sub>3</sub> which is a V<sub>62</sub>VI<sub>33</sub> type stoichiometric compound. As expected from the pseudo-binary phase diagram of Fig. 2, since there is no possibility of forming SnTe which is a IV<sub>6</sub>VI<sub>6</sub> type stoichiometric compound having a high melting point upon crystal-amorphous phase transition, recorded information hardly remains non-erased even when recording is conducted with a low laser power, and the

recording medium exhibited satisfactory stability on repetition of rewriting.

#### EXAMPLE 2

5

Optical recording media were prepared in the same manner as in Example 1, except that the recording material layer was composed of Sn-Sb-Se.

10 The Sn-Sb-Se recording material was formed by binary simultaneous sputtering using two alloy targets of SnSe and  $\text{Sb}_2\text{Se}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 5 below.

15

#### EXAMPLE 3

Optical recording media were prepared in the same manner as in Example 1, except that the recording material layer was composed of Pb-Sb-Te.

20 The Pb-Sb-Te recording material was formed by binary simultaneous sputtering using two alloy targets of PbTe and  $\text{Sb}_2\text{Te}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 5 below.

25

#### EXAMPLE 4

30 Optical recording media were prepared in the same manner as in Example 1, except that the recording material layer was composed of Pb-Bi-Te.

The Pb-Bi-Te recording material was formed by binary simultaneous sputtering using two alloy targets of PbTe and  $\text{Bi}_2\text{Te}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 5 below.

35

#### EXAMPLE 5

40 Optical recording media were prepared in the same manner as in Example 1, except that the recording material layer was composed of Pb-Bi-Se.

The Pb-Bi-Se recording material was formed by binary simultaneous sputtering using two alloy targets of PbSe and  $\text{Bi}_2\text{Se}_3$ .

45 Recording and erasure characteristics of the resulting optical recording media are shown in Table 5 below.

50

55

TABLE 5

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
2	6	(SnSe) <sub>30</sub> (Sb <sub>2</sub> Se <sub>3</sub> ) <sub>70</sub>	good	good
"	7	(SnSe) <sub>40</sub> (Sb <sub>2</sub> Se <sub>3</sub> ) <sub>60</sub>	good	good
"	8	(SnSe) <sub>67</sub> (Sb <sub>2</sub> Se <sub>3</sub> ) <sub>33</sub>	good	good
3	9	(PbTe) <sub>30</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>70</sub>	good	good
"	10	(PbTe) <sub>40</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub>	good	good
"	11	(PbTe) <sub>50</sub> (Sb <sub>2</sub> Te <sub>3</sub> ) <sub>50</sub>	good	good
4	12	(PbTe) <sub>25</sub> (Bi <sub>2</sub> Te <sub>3</sub> ) <sub>75</sub>	good	good
"	13	(PbTe) <sub>33</sub> (Bi <sub>2</sub> Te <sub>3</sub> ) <sub>67</sub>	good	good
"	14	(PbTe) <sub>40</sub> (Bi <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub>	good	good
5	15	(PbSe) <sub>33</sub> (Bi <sub>2</sub> Se <sub>3</sub> ) <sub>67</sub>	good	good
"	16	(PbSe) <sub>50</sub> (Bi <sub>2</sub> Se <sub>3</sub> ) <sub>50</sub>	good	good

As is apparent from Table 5, Samples 6 to 16 according to the present invention have a reduced time of crystallization, making it possible to conduct recording and erasure of information at a higher speed, and also have an increased crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Comparative Example 1, similarly to Samples 1 to 3 of Example 1.

In particular, as anticipated from the pseudo-binary phase diagrams of Figs. 3 to 6, it was confirmed that the crystal phase of the recording material in Samples 7, 8, 10, 13, 15, and 16 is composed of a single phase of a stoichiometric compound, i.e., Sn<sub>2</sub>Sb<sub>5</sub>Se<sub>11</sub>, Sn<sub>2</sub>Sb<sub>2</sub>Se<sub>5</sub>, Pb<sub>2</sub>Sb<sub>5</sub>Te<sub>11</sub>, PbBi<sub>4</sub>Te<sub>7</sub> (shown as PbTe.2Bi<sub>2</sub>Te<sub>3</sub> in the figures), PbBi<sub>4</sub>Se<sub>7</sub> (shown as PbSe.2Bi<sub>1</sub>Se<sub>3</sub> in figures), and PbBi<sub>2</sub>Se<sub>4</sub> (shown as PbSe.Bi<sub>2</sub>Se<sub>3</sub> in figures), respectively. Therefore, these samples had a short crystallization time and exhibited satisfactory stability on repetition of rewriting similarly to Sample 2 of Example 1.

Further, as can be seen from the respective phase diagram, since Sn<sub>2</sub>Sb<sub>5</sub>Se<sub>11</sub> of Sample 7, Pb<sub>2</sub>Sb<sub>5</sub>Te<sub>11</sub> of Sample 10, and PbBi<sub>4</sub>Te<sub>7</sub> of Sample 13 are congruent compounds, recording layers of these materials suffer from no local crystallization and exhibit satisfactory characteristics on repetition of rewriting.

The recording materials of Samples 6, 9, and 12 have a composition corresponding to a mixture of a congruent compound Sn<sub>2</sub>Sb<sub>5</sub>Se<sub>11</sub> and a V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound Sb<sub>2</sub>Se<sub>3</sub>, a mixture of a congruent compound Pb<sub>2</sub>Sb<sub>5</sub>Te<sub>11</sub> and a V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound Sb<sub>2</sub>Te<sub>3</sub>, and a mixture of a congruent compound PbBi<sub>4</sub>Te<sub>7</sub> and a V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound Bi<sub>2</sub>Te<sub>3</sub>, respectively. As expected from the respective pseudo-binary diagram shown in Figs. 3 to 5, since there is no possibility of forming SnSe or PbTe, which is a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound, having a high melting point at the time of crystal-amorphous phase transition, recorded information hardly remains non-erased even when recording is conducted with a low laser power, and the recording medium exhibited satisfactory stability on repetition of rewriting.

It is apparent from Examples 1 to 5 that use of recording material (i) according to the present invention increases stability of the recording material layer in its amorphous phase and reduces the time of crystallization of the recording material layer. The optical recording media using recording material (i) are thus capable of rewriting at a high speed and maintaining recorded information for an extended period of time.

The optical recording media using recording material (ii) according to the present invention likewise have increased stability in the amorphous phase of the recording material layer and a reduced crystallization time of the recording material layer. Besides, IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compounds having a high melting point are not formed on crystal-amorphous phase transition. Therefore, the optical recording media using recording material (ii) are not only capable of rewriting at a high speed and maintaining recorded information for an extended period of time similarly to those using recording material (i) but also do not suffer from incomplete erasure of recorded information even when recording and erasure are carried out with a low laser power while retaining such excellent recording characteristics on repeated use.

Because recording materials (i) and (ii) show absorption of visible and near infrared light due to the presence of at least one of Se and Te, widespread light sources inclusive of semi-conductor lasers can be applied to these materials.

Where the crystal phase of recording materials is comprised of a single phase of a stoichiometric

compound, the free energy of the crystal phase is further reduced, which leads to further reduction of the crystallization time. In addition, because such a crystal phase does not suffer from phase separation, the recording characteristics remain unchanged even rewriting is conducted many times.

Where the stoichiometric compound is composed of a congruent compound, local crystallization does not take place during cooling so that unchangeability of the recording characteristics on repeated use is further ensured.

#### EXAMPLE 6

Optical recording media having a structure shown in Fig. 1 were prepared, each comprising 1.2 mm-thick acrylic resin substrate (1) having thereon 100 nm-thick inorganic dielectric material layer (2) made of  $\text{SiO}_2$ , 100 nm-thick recording material layer (3) made of Li-Sb-Se, 100 nm-thick inorganic dielectric material layer (4) made of  $\text{SiO}_2$ , ultraviolet curable acrylic resin adhesive layer (5), and 1.2 mm-thick acrylic resin protective layer (6) in this order.

Recording material layer (3) was formed by sputtering using an RF magnetron and two alloy targets,  $\text{Li}_2\text{Se}$  and  $\text{Sb}_2\text{Se}_3$  while appropriately controlling the RF power to the respective alloy target so as to synthesize a composition shown in Table 6 below. The resulting optical recording media were designated Samples 17 and 18.

Samples 17 and 18 showed absorption in the wavelength region of from visible light to near infrared light and could be used as optical recording media at least in the wavelength region of from 400 nm to 860 nm.

Recording and erasure characteristics when these recording media were used by using a semiconductor laser having a wavelength of 830 nm as a light source are also shown in Table 6.

TABLE 6

Sample No.	Composition of Recording Material	Time of Crystallization	Stability
17	$(\text{Li}_2\text{Se})_{50}(\text{Sb}_2\text{Se}_3)_{50}$	good	good
18	$(\text{Li}_2\text{Se})_{40}(\text{Sb}_2\text{Se}_3)_{60}$	good	good

As is apparent from Table 6, Samples 17 and 18 have a reduced time of crystallization, making it possible to conduct recording and erasure of information at a higher speed, as compared with Sample 5 of Comparative Example 1 and also have an increased crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Sample 4 of Comparative Example 1.

In particular, it was confirmed that the crystal phase of Li-Sb-Se in Sample 17 is a single phase composed of a congruent compound as expected from the pseudo-binary phase diagram of Fig. 7, i.e.,  $\text{LiSbSe}_2$ . Therefore, the recording material had a short crystallization time and exhibited satisfactory stability on repetition of rewriting.

#### EXAMPLE 7

Optical recording media (Samples 19 and 20) were prepared in the same manner as in Example 6, except that the recording material layer was composed of Na-Sb-Se.

The Na-Sb-Se recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{Na}_2\text{Se}$  and  $\text{Sb}_2\text{Se}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.

#### EXAMPLE 8

Optical recording media were prepared in the same manner as in Example 6, except that the recording material layer was composed of Cu-Sb-Se.

The Cu-Sb-Se recording material was formed by binary simultaneous sputtering using a single target prepared by mixing  $\text{Cu}_2\text{Se}$  and  $\text{Sb}_2\text{Se}_3$  at a ratio of 60:40 (Sample 21), 50:50 (Sample 22), or 40:60 (Sample 23).

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.

#### EXAMPLE 9

Optical recording media (Samples 24 to 26) were prepared in the same manner as in Example 6, except that the recording material layer was composed of Cu-In-Te.

The Cu-In-Te recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{Cu}_2\text{Te}$  and  $\text{In}_2\text{Te}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.

#### EXAMPLE 10

Optical recording media (Samples 27 to 29) were prepared in the same manner as in Example 6, except that the recording material layer was composed of Ag-In-Te.

The Ag-In-Te recording material was formed by binary simultaneous sputtering using a single target prepared by mixing  $\text{Ag}_2\text{Te}$  and  $\text{In}_2\text{Te}_3$  at a ratio of 60:40 (Sample 27), 50:50 (Sample 28), or 40:60 (Sample 29).

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.

#### EXAMPLE 11

A optical recording medium (Sample 30) was prepared in the same manner as in Example 6, except that the recording material layer was composed of Ag-In-Se.

The Ag-In-Se recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{Ag}_2\text{Se}$  and  $\text{In}_2\text{Se}_3$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.

#### EXAMPLE 12

Optical recording media (Samples 31 to 33) were prepared in the same manner as in Example 6, except that the recording material layer was composed of Cu-Sn-Se.

The Cu-Sn-Se recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{Cu}_2\text{Se}$  and  $\text{SnS}_2$ .

Recording and erasure characteristics of the resulting optical recording media are shown in Table 7 below.



TABLE 7

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 7	19	$(\text{Na}_2\text{Se})_{50}(\text{Sb}_2\text{Se}_3)_{50}$	good	good
"	20	$(\text{Na}_2\text{Se})_{40}(\text{Sb}_2\text{Se}_3)_{60}$	good	good
Example 8	21	$(\text{Cu}_2\text{Se})_{60}(\text{Sb}_2\text{Se}_3)_{40}$	good	good
"	22	$(\text{Cu}_2\text{Se})_{50}(\text{Sb}_2\text{Se}_3)_{50}$	good	good
"	23	$(\text{Cu}_2\text{Se})_{40}(\text{Sb}_2\text{Se}_3)_{60}$	good	good
Example 9	24	$(\text{Cu}_2\text{Te})_{55}(\text{In}_2\text{Te}_3)_{45}$	good	good
"	25	$(\text{Cu}_2\text{Te})_{50}(\text{In}_2\text{Te}_3)_{50}$	good	good
"	26	$(\text{Cu}_2\text{Te})_{45}(\text{In}_2\text{Te}_3)_{55}$	good	good
Example 10	27	$(\text{Ag}_2\text{Te})_{60}(\text{In}_2\text{Te}_3)_{40}$	good	good
"	28	$(\text{Ag}_2\text{Te})_{50}(\text{In}_2\text{Te}_3)_{50}$	good	good
"	29	$(\text{Ag}_2\text{Te})_{40}(\text{In}_2\text{Te}_3)_{60}$	good	good
Example 11	30	$(\text{Ag}_2\text{Se})_{17}(\text{In}_2\text{Se}_3)_{83}$	good	good
Example 12	31	$(\text{Cu}_2\text{Se})_{40}(\text{SnSe}_2)_{60}$	good	good
"	32	$(\text{Cu}_2\text{Se})_{50}(\text{SnSe}_2)_{50}$	good	good
"	33	$(\text{Cu}_2\text{Se})_{60}(\text{SnSe}_2)_{40}$	good	good

As is apparent from Table 7, Samples 19 to 33 have a reduced time of crystallization, making it possible to conduct recording and erasure of information at a higher speed, and also have a higher crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Comparative Example 1, similarly to Samples 17 and 18 of Example 6.

As expected from the pseudo-binary phase diagrams of Figs. 8 to 13, it was confirmed that the crystal phase of Na-Sb-Se in Sample 19, Cu-Sb-Se in Sample 22, Cu-In-Te in Sample 25, Ag-In-Te in Sample 28, Ag-In-Se in Sample 30, and Cu-Sn-Se in Sample 32 is a single phase composed of a stoichiometric compound which is stable at room temperature, i.e.,  $\text{NaSbSe}_2$ ,  $\text{CuSbSe}_2$ ,  $\text{CuInTe}_2$ ,  $\text{AgInTe}_2$ ,  $\text{AgIn}_5\text{Se}_8$ , and  $\text{Cu}_2\text{SnSe}_3$ , respectively. In particular,  $\text{AgIn}_5\text{Se}_8$  of Sample 30 and  $\text{Cu}_2\text{SnSe}_3$  of Sample 32 are congruent compounds and, therefore, these samples had a short crystallization time and exhibited satisfactory stability on repetition of rewriting.

It is apparent from Examples 6 to 12 that use of recording material (iii) according to the present invention reduces the time of crystallization of the recording material layer and increases stability of the recording material layer in its amorphous phase.

The optical recording media using recording material (iii) are thus capable of rewriting at a high speed and maintaining recorded information for an extended period of time.

Because recording material (iii) shows absorption of visible and near infrared light due to the presence of at least one of Se and Te, widespread light sources inclusive of semi-conductor lasers can be applied to the optical recording media using recording material (iii).

Where the crystal phase of recording material (iii) is a single phase composed of a stoichiometric compound, the free energy of the crystal phase is further reduced, which leads to further reduction of the crystallization time. In addition, because such a crystal phase does not suffer from phase separation, the recording characteristics remain unchanged even rewriting is conducted many times.

Where the above-described stoichiometric compound is composed of a congruent compound, local crystallization does not take place during cooling so that unchangeability of the recording characteristics on repeated use is further ensured.

### EXAMPLE 13

Optical recording media having a structure shown in Fig. 1 were prepared, each comprising 1.2 mm-thick acrylic resin substrate (1) having thereon 100 nm-thick inorganic dielectric material layer (2) made of  $\text{SiO}_2$ , 100 nm-thick recording material layer (3) made of Ga-Ge-Te, 100 nm-thick inorganic dielectric material layer (4) made of  $\text{SiO}_2$ , ultraviolet curable acrylic resin adhesive layer (5), and 1.2 mm-thick acrylic resin protective layer (6) in this order.

Recording material layer (3) was formed by sputtering using an RF magnetron and two alloy targets, GaTe and GeTe while appropriately controlling the RF power to the respective alloy target so as to synthesize a composition shown in Table 8 below. The resulting optical recording media were designated Samples 34 to 36.

Samples 34 to 36 showed absorption in the wavelength region of from visible light to near infrared light and could be used as optical recording media at least in the wavelength region of from 400 nm to 860 nm.

Recording and erasure characteristics when these recording media were used by using a semiconductor laser having a wavelength of 830 nm as a light source are also shown in Table 8.

TABLE 8

Sample No.	Composition of Recording Material	Time of Crystallization	Stability
34	(GaTe) <sub>50</sub> (GeTe) <sub>50</sub>	good	good
35	(GaTe) <sub>60</sub> (GeTe) <sub>40</sub>	good	good
36	(GaTe) <sub>67</sub> (GeTe) <sub>33</sub>	good	good

As is apparent from Table 8, Samples 34 to 36 have a reduced time of crystallization as compared with Sample 5 of Comparative Example 1, making it possible to conduct recording and erasure of information at a higher speed, and also have a higher crystallization temperature as compared with Sample 4 of Comparative Example 1, indicating improved stability of the amorphous phase.

As expected from the pseudo-binary phase diagrams of Fig. 14, it was confirmed that the crystal phase of Ga-Ge-Te in Samples 34 and 36 is a single phase composed of a stoichiometric compound which is stable at room temperature, i.e., GaGeTe<sub>2</sub> and Ga<sub>2</sub>GeTe<sub>3</sub>, respectively. In particular, GaGeTe<sub>2</sub> of Sample 34 is a congruent compound and, therefore, the sample had a shorter crystallization time and exhibited higher stability on repetition of rewriting.

#### EXAMPLE 14

Optical recording media (Samples 37 and 39) were prepared in the same manner as in Example 13, except that the recording material layer was composed of In-Ge-Te.

The In-Ge-Te recording material was formed by binary simultaneous sputtering using a single target obtained by mixing InTe and GeTe at a ratio of 50:50 (Sample 37), 60:40 (Sample 38) or 67:33 (Sample 39).

Recording and erasure characteristics of the resulting optical recording media are shown in Table 9 below.

#### EXAMPLE 15

An optical recording medium was prepared in the same manner as in Example 13, except that the recording material layer was composed of In-Sn-Te.

The In-Sn-Te recording material was formed by binary simultaneous sputtering using two alloy targets of InTe and SnTe.

Recording and erasure characteristics of the resulting optical recording media are shown in Table 9 below.

#### EXAMPLE 16

Optical recording media (Samples 41 to 42) were prepared in the same manner as in Example 13, except that the recording material layer was composed of In-Pb-Te.

The In-Pb-Te recording material was formed by binary simultaneous sputtering using two alloy targets of InTe and PbTe.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

5

#### EXAMPLE 17

10 Optical recording media (Samples 43 to 45) were prepared in the same manner as in Example 13, except that the recording material layer was composed of Tl-Ge-Te.

The Tl-Ge-Te recording material was formed by binary simultaneous sputtering using two alloy targets of TlTe and GeTe.

15 Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

#### EXAMPLE 18

20

Optical recording media (Samples 46 to 48) were prepared in the same manner as in Example 13, except that the recording material layer was composed of Ga-Tl-Se.

The Ga-Tl-Se recording material was formed by binary simultaneous sputtering using a single target prepared by mixing GaSe and TeSe at a ratio of 40:60 (Sample 46), 50:50 (Sample 47), or 60:40 (Sample 25 48).

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

30

#### EXAMPLE 19

Optical recording media (Samples 49 to 51) were prepared in the same manner as in Example 13, except that the recording material layer was composed of In-Tl-Se.

35 The In-Tl-Se recording material was formed by binary simultaneous sputtering using two alloy targets of InSe and TlSe.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

40

#### EXAMPLE 20

Optical recording media (Samples 52 to 54) were prepared in the same manner as in Example 13, 45 except that the recording material layer was composed of Ga-Se-Te.

The Ga-Se-Te recording material was formed by binary simultaneous sputtering using two alloy targets of GaSe and GaTe.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 50 below.

50

#### EXAMPLE 21

55 Optical recording media (Samples 55 to 57) were prepared in the same manner as in Example 13, except that the recording material layer was composed of In-S-Te.

The In-S-Te recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{In}_2\text{S}_3$  and  $\text{In}_2\text{Te}_3$ .

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

### EXAMPLE 22

Optical recording media (Samples 58 to 59) were prepared in the same manner as in Example 13, except that the recording material layer was composed of Ga-Sn-Te.

The Ga-Sn-Te recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{Ga}_2\text{Te}_3$  and  $\text{SnTe}$ .

Recording and erasion characteristics of the resulting optical recording media are shown in Table 9 below.

### EXAMPLE 23

A optical recording medium (Sample 60) was prepared in the same manner as in Example 13, except that the recording material layer was composed of Ga-Ge-Se.

The Ga-Ge-Se recording material was formed by binary simultaneous sputtering using two alloy targets of  $\text{GaSe}$  and  $\text{GeSe}_2$ .

Recording and erasion characteristics of the resulting optical recording medium are shown in Table 9 below.

TABLE 9

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 14	37	$(\text{InTe})_{50}(\text{GeTe})_{50}$	good	good
"	38	$(\text{InTe})_{60}(\text{GeTe})_{40}$	good	good
"	39	$(\text{InTe})_{67}(\text{GeTe})_{33}$	good	good
Example 15	40	$(\text{InTe})_{75}(\text{PbTe})_{20}$	good	good
Example 16	41	$(\text{InTe})_{50}(\text{PbTe})_{50}$	good	good
"	42	$(\text{InTe})_{60}(\text{PbTe})_{40}$	good	good
Example 17	43	$(\text{TlTe})_{50}(\text{GeTe})_{50}$	good	good
"	44	$(\text{TlTe})_{60}(\text{GeTe})_{40}$	good	good
"	45	$(\text{TlTe})_{67}(\text{GeTe})_{33}$	good	good
Example 18	46	$(\text{GaSe})_{40}(\text{TlSe})_{60}$	good	good
"	47	$(\text{GaSe})_{50}(\text{TlSe})_{50}$	good	good
"	48	$(\text{GaSe})_{60}(\text{TlSe})_{40}$	good	good

/To be cont'd.

TABLE 9 (cont'd.)

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 19	49	(InSe) <sub>40</sub> (TlSe) <sub>60</sub>	good	good
"	50	(InSe) <sub>50</sub> (TlSe) <sub>50</sub>	good	good
"	51	(InSe) <sub>60</sub> (TlSe) <sub>40</sub>	good	good
Example 20	52	(GaSe) <sub>40</sub> (GaTe) <sub>60</sub>	good	good
"	53	(GaSe) <sub>50</sub> (GaTe) <sub>50</sub>	good	good
"	54	(GaSe) <sub>60</sub> (GaTe) <sub>40</sub>	good	good
Example 21	55	(In <sub>2</sub> S <sub>3</sub> ) <sub>40</sub> (In <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub>	good	good
"	56	(In <sub>2</sub> S <sub>3</sub> ) <sub>33</sub> (In <sub>2</sub> Te <sub>3</sub> ) <sub>67</sub>	good	good
"	57	(In <sub>2</sub> S <sub>3</sub> ) <sub>25</sub> (In <sub>2</sub> Te <sub>3</sub> ) <sub>75</sub>	good	good
Example 22	58	(Ga <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub> (SnTe) <sub>40</sub>	good	good
"	59	(Ga <sub>2</sub> Te <sub>3</sub> ) <sub>67</sub> (SnTe) <sub>33</sub>	good	good
Example 23	60	(GaSe) <sub>50</sub> (GeSe <sub>2</sub> ) <sub>50</sub>	good	good

As is apparent from Table 9, Samples 37 to 60 have a reduced time of crystallization, making it possible to conduct recording and erasure of information at a higher speed, and also have a higher crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Comparative Example 1, similarly to Samples 34 to 36 of Example 13.

As expected from the pseudo-binary phase diagrams of Figs. 15 to 23, it was confirmed that the crystal phase of In-Ge-Te in Samples 37 and 39, In-Sn-Te in Sample 40, In-Pb-Te in Sample 41, Tl-Ge-Te in Samples 43 and 45, Ga-Tl-Se in Sample 47, In-Tl-Se in Sample 50, Ga-Se-Te in Sample 53, In-S-Te in Sample 56, and Ga-Sn-Te in Sample 59 is a single phase composed of a stoichiometric compound which is stable at room temperature, i.e., InGeTe<sub>2</sub>, In<sub>2</sub>GeTe<sub>3</sub>, In<sub>3</sub>SnTe<sub>4</sub>, InPbTe<sub>2</sub>, TlGeTe<sub>2</sub>, Tl<sub>2</sub>GeTe<sub>3</sub>, TlGaSe<sub>2</sub>, TlInSe<sub>2</sub>, Ga<sub>2</sub>SeTe, In<sub>2</sub>STe<sub>2</sub>, and Ga<sub>4</sub>SnTe<sub>7</sub>, respectively. In particular, InGeTe<sub>2</sub> of Sample 37, TlGaSe<sub>2</sub> of Sample 47, TlInSe<sub>2</sub> of Sample 50, Ga<sub>2</sub>SeTe of Sample 53, and In<sub>2</sub>STe<sub>2</sub> of Sample 56 are congruent compounds and, therefore, these samples had a short crystallization time and exhibited satisfactory stability on repetition of rewriting.

Further, the crystal phase of Ga-Ge-Se of Sample 60 is also composed of a stoichiometric compound stable at room temperature as represented by GaGeSe<sub>3</sub>, and the sample had a short crystallization time and exhibited satisfactory stability on repetition of rewriting.

It is apparent from Examples 13 to 23 that use of recording material (iv) or (v) according to the present invention reduces the time of crystallization of the recording material layer and increases stability of the recording material layer in its amorphous phase.

The optical recording media using these recording materials are thus capable of rewriting at a high speed and maintaining recorded information for an extended period of time.

Because recording materials (iv) and (v) show absorption of visible and near infrared light due to the presence of at least one of Se and Te, widespread light sources inclusive of semi-conductor lasers can be applied to the optical recording media using these recording materials.

Where the crystal phase of the recording material is a single phase composed of a stoichiometric compound, the free energy of the crystal phase is further reduced, which leads to further reduction of the

crystallization time. In addition, because such a crystal phase does not suffer from phase separation, the recording characteristics remain unchanged even rewriting is conducted many times.

Where the above-described stoichiometric compound is composed of a congruent compound, local crystallization does not take place during cooling so that unchangeability of the recording characteristics on repeated use is further ensured.

#### EXAMPLE 24 AND COMPARATIVE EXAMPLE 2

10

Optical recording media (Samples 61 to 62) having a structure shown in Fig. 1 were prepared, each comprising 1.2 mm-thick acrylic resin substrate (1) having thereon 100 nm-thick inorganic dielectric material layer (2) made of  $\text{SiO}_2$ , 100 nm-thick recording material layer (3) made of Sn-Sb-Bi-Te (Sample 61) or Sn-Sb-Se-Te (Sample 62), 100 nm-thick inorganic dielectric material layer (4) made of  $\text{SiO}_2$ , ultraviolet curable acrylic resin adhesive layer (5), and 1.2 mm-thick acrylic resin protective layer (6) in this order.

Recording material layer (3) was formed by sputtering using an RF magnetron and two alloy targets of  $(\text{SnSb}_2\text{Te}_4)$  and  $(\text{SnBi}_2\text{Te}_4)$  or two alloy targets of  $(\text{SnSb}_2\text{Te}_4)$  and  $(\text{SnSe}_2\text{Te}_4)$ , respectively, while appropriately controlling the RF power to the respective alloy target so as to obtain a four-element solid solution having a composition shown in Table 10 below. In Sample 61,  $(\text{SnSb}_2\text{Te}_4)$  and  $(\text{SnBi}_2\text{Te}_4)$  were used at a ratio of 45:55, and in Sample 62,  $(\text{SnSb}_2\text{Te}_4)$  and  $(\text{SnSe}_2\text{Te}_4)$  were used at a ratio of 74:26.

Comparative Samples 63 and 64 were prepared by using as a recording material Ge-Sb-Te or Sn-Sb-Te, respectively, with the layer structure being the same as Samples 61 and 62. (Comparative Example 2) The recording material layer of Samples 63 or 64 was formed by RF magnetron sputtering using two alloy targets of  $\text{Sb}_2\text{Te}_3$  and GeTe at a ratio of 67:33 or two alloy targets of  $\text{Sb}_2\text{Te}_3$  and SnTe at a ratio of 50:50, respectively.

Samples 61 to 64 showed absorption in the wavelength region of from visible light to near infrared light and could be used as optical recording media at least in the wavelength region of from 400 nm to 860 nm.

Recording and erasure characteristics when these recording media were used by using a semiconductor laser having a wavelength of 830 nm as a light source are also shown in Table 10. In Table 10, stability was rated according to the following standards.

Standards for Evaluation:

Excellent ... Crystallization temperature is higher than  $160^\circ\text{C}$ .

Good ... Crystallization temperature is from  $120^\circ\text{C}$  to  $160^\circ\text{C}$ .

Poor ... Crystallization temperature is less than  $120^\circ\text{C}$ .

35

TABLE 10

40

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 24	61	$\text{Sn}_{1.4}\text{Sb}_{1.3}\text{Bi}_{1.6}\text{Te}_{5.7}$	good	excellent
"	62	$\text{Sn}_{1.4}\text{Sb}_{2.9}\text{Se}_{1.5}\text{Te}_{4.2}$	good	excellent
Comparative Example 2	63	$\text{Ge}_8\text{Sb}_{3.4}\text{Te}_{5.8}$	poor	good
"	64	$\text{Sn}_{1.4}\text{Sb}_{2.9}\text{Te}_{5.7}$	good	good

45

As is apparent from Table 10, Samples 61 and 62 according to the present invention have a reduced time of crystallization as compared with Sample 63 of Comparative Example 2, making it possible to conduct recording and erasure of information at a higher speed, and also have a higher crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Sample 64 of Comparative Example 2 and Sample 4 of Comparative Example 1 (see Table 4).

The recording material in Samples 61 or 62 is a four-element solid solution having a composition corresponding to a structure obtained by partly substituting Sb and Te in  $\text{SnSb}_2\text{Te}_4$  of Sample 64 whose pseudo-binary phase diagram is shown in Fig. 24 by Bi or Se, respectively (Bi or Se and the elements to be substituted can form a full-range solid solution). The results of Table 10 proved that the stability of the amorphous phase can be ensured by such partial substitution.

EXAMPLE 25

5 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of Li-Sb-Se-Te.

The Li-Sb-Se-Te recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{Li}_{25}\text{Sb}_{25}\text{Se}_{30}\text{Te}_{20}$ .

10 The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Se, a constituent element of  $\text{LiSbSe}_2$  whose pseudo-binary phase diagram is shown in Fig. 25, by Te which can form a full-range solid solution with Se.

Recording and erasure characteristics of the resulting optical recording medium are shown in Table 11 below.

EXAMPLE 26

15 A optical recording medium (Sample 66 or 67) was prepared in the same manner as in Example 24, except that the recording material layer was composed of Ag-In-Tl-Te or Ag-In-Tl-Se-Te, respectively.

20 The Ag-In-Tl-Te recording material layer of Sample 66 was a four-element solid solution formed by simultaneous sputtering using three alloy targets of (AgTe), (InTe), and (TlTe) at a ratio of 50:40:10. The Ag-In-Tl-Se-Te recording material layer of Sample 67 was a five-element solid solution formed by simultaneous sputtering using three alloy targets of (AgTe), (InTe), and (TlSe) at a ratio of 50:40:10.

25 The four-element solid solution of Sample 66 had a structure obtained by partly substituting In, a constituent element of  $\text{AgInTe}_2$  whose pseudo-binary phase diagram is shown in Fig. 26, by Tl. On the other hand, the five-element solid solution of Sample 67 had a structure obtained by partly substituting In and Te, constituent elements of  $\text{AgInTe}_2$  whose pseudo-binary phase diagram is shown in Fig. 26, by Tl and Se which can form a full-range solid solution with Te.

30 Recording and erasure characteristics of the resulting optical recording media are shown in Table 11 below.

EXAMPLE 27

35 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of Cu-Au-Sn-Se.

The Cu-Au-Sn-Se recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{Cu}_{27}\text{Au}_{25}\text{Sn}_{13}\text{Se}_{37}$ .

40 The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Cu, a constituent element of  $\text{Cu}_2\text{SnSe}_3$  whose pseudo-binary phase diagram is shown in Fig. 27, by Au.

Recording and erasure characteristics of the resulting optical recording medium are shown in Table 11 below.

EXAMPLE 28

50 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of In-Ge-Se-Te.

The In-Ge-Se-Te recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{In}_{25}\text{Ge}_{25}\text{Se}_{13}\text{Te}_{37}$ .

55 The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Te, a constituent element of  $\text{InGeTe}_2$  whose pseudo-binary phase diagram is shown in Fig. 28, by Se which can form a full-range solid solution with Te.

Recording and erasure characteristics of the resulting optical recording medium are shown in Table 11 below.

EXAMPLE 29

5 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of Ga-Tl-Ge-Se.

The Ga-Tl-Ge-Se recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{Ga}_{15}\text{Tl}_5\text{Ge}_{20}\text{Se}_{60}$ .

The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Ga, a constituent element of  $\text{GaGeSe}_3$ , by Tl.

10 Recording and erasion characteristics of the resulting optical recording medium are shown in Table 11 below.

EXAMPLE 30

15 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of In-Tl-Se-Te.

The In-Tl-Se-Te recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{In}_{25}\text{Tl}_{25}\text{Se}_{30}\text{Te}_{20}$ .

The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Se, a constituent element of  $\text{InTlSe}_2$  whose pseudo-binary phase diagram is shown in Fig. 29, by Te which can form a full-range solid solution with Se.

25 Recording and erasion characteristics of the resulting optical recording medium are shown in Table 11 below.

EXAMPLE 31

30 A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of In-S-Se-Te.

The In-S-Se-Te recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{In}_{40}\text{S}_{20}\text{Se}_{13}\text{Te}_{27}$ .

35 The four-element solid solution had a composition corresponding to a structure obtained by partly substituting Te, a constituent element of  $\text{In}_2\text{STe}_2$  whose pseudo-binary phase diagram is shown in Fig. 30, by Se which can form a full-range solid solution with Te.

Recording and erasion characteristics of the resulting optical recording medium are shown in Table 11 below.

40

EXAMPLE 32

45 A optical recording medium (Sample 73 or 74) was prepared in the same manner as in Example 24, except that the recording material layer was composed of Ga-Tl-Sn-Te or Ga-Sn-Se-Te, respectively.

The Ga-Tl-Sn-Te recording material layer of Sample 73 was formed by sputtering using a single target of a four-element solid solution having a composition of  $\text{Ga}_{29}\text{Tl}_5\text{Sn}_8\text{Te}_{58}$ . The Ga-Sn-Se-Te recording material layer of Sample 74 was formed by sputtering using a single target of a four-element solid solution

50 having a composition of  $\text{Ga}_{34}\text{Sn}_8\text{Se}_{15}\text{Te}_{43}$ .

The four-element solid solution of Sample 73 had a structure obtained by partly substituting Ga, a constituent element of  $\text{Ga}_4\text{SnTe}_7$  whose pseudo-binary phase diagram is shown in Fig. 31, by Tl. On the other hand, the four-element solid solution of Sample 74 had a structure obtained by partly substituting Te, a constituent element of  $\text{Ga}_4\text{SnTe}_7$  whose pseudo-binary phase diagram is shown in Fig. 31, by Se which

55 can form a full-range solid solution with Te.

Recording and erasion characteristics of the resulting optical recording medium are shown in Table 11 below.



EXAMPLE 33

A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of Pb-Bi-S-Se-Te.

The Pb-Bi-S-Se-Te recording material layer was a five-element solid solution formed by simultaneous sputtering using three alloy targets of (PbSe), (Bi<sub>2</sub>Se<sub>3</sub>), and (Bi<sub>2</sub>STe<sub>2</sub>) at a ratio of 33:51:16.

The five-element solid solution had a structure obtained by partly substituting Se, a constituent element of PbBi<sub>4</sub>Se<sub>7</sub> whose pseudo-binary phase diagram is shown in Fig. 32, by S and Te.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 11 below.

EXAMPLE 34

A optical recording medium was prepared in the same manner as in Example 24, except that the recording material layer was composed of Cu-Tl-Sb-Se.

The Cu-Tl-Sb-Se recording layer was formed by sputtering using a single target of a four-element solid solution having a composition of Cu<sub>20</sub>Tl<sub>5</sub>Sb<sub>25</sub>Se<sub>50</sub>.

The four-element solid solution had a structure obtained by partly substituting Cu of the group Ib, a constituent element of CuSbSe<sub>2</sub> whose pseudo-binary phase diagram is shown in Fig. 33, by Tl of the group IIIb.

Recording and erasion characteristics of the resulting optical recording medium are shown in Table 11 below.

TABLE 11

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
Example 25	65	Li <sub>25</sub> Sb <sub>25</sub> Se <sub>30</sub> Te <sub>20</sub>	good	excellent
" 26	66	Ag <sub>25</sub> In <sub>20</sub> Tl <sub>5</sub> Te <sub>50</sub>	good	excellent
" 26	67	Ag <sub>25</sub> In <sub>20</sub> Tl <sub>5</sub> Se <sub>5</sub> Te <sub>50</sub>	good	excellent
" 27	68	Cu <sub>27</sub> Au <sub>6</sub> Sn <sub>17</sub> Se <sub>50</sub>	good	excellent
" 28	69	In <sub>25</sub> Ge <sub>25</sub> Se <sub>13</sub> Te <sub>37</sub>	good	excellent
" 29	70	Ga <sub>15</sub> Tl <sub>5</sub> Ge <sub>20</sub> Se <sub>60</sub>	good	excellent
" 30	71	In <sub>25</sub> Tl <sub>25</sub> Se <sub>30</sub> Te <sub>20</sub>	good	excellent
" 31	72	In <sub>40</sub> S <sub>20</sub> Se <sub>13</sub> Te <sub>27</sub>	good	excellent
" 32	73	Ga <sub>29</sub> Tl <sub>5</sub> Sn <sub>8</sub> Te <sub>58</sub>	good	excellent
" 32	74	Ga <sub>34</sub> Sn <sub>8</sub> Se <sub>15</sub> Te <sub>43</sub>	good	excellent
" 33	75	Pb <sub>8</sub> Bi <sub>33</sub> S <sub>4</sub> Se <sub>47</sub> Te <sub>8</sub>	good	excellent
" 34	76	Cu <sub>20</sub> Tl <sub>5</sub> Sb <sub>25</sub> Se <sub>50</sub>	good	excellent

As is apparent from Table 11, Samples 65 to 76 according to the present invention have a reduced time of crystallization, making it possible to conduct recording and erasion of information at a higher speed, and also have a higher crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Comparative Examples 1 and 2, similarly to Samples 61 and 62 of Example 24.

The four-element solid solution and five-element solid solution in Samples 66 and 67 both have a structure obtained by partly substituting In, a constituting element of AgInTe<sub>2</sub> whose pseudo-binary phase diagram is shown in Fig. 26, by Tl, and exhibit accelerated crystallization by the action of Tl.

Likewise, the four-element solid solutions of Samples 70, 73, and 76 possess a structure obtained by partly substituting Ga of GaGeSe<sub>3</sub>, Ga of Ga<sub>4</sub>SnTe<sub>7</sub>, or Cu of CuSbSe<sub>2</sub>, respectively, by Tl and, hence, exhibited accelerated crystallization.

As is obvious from Examples 24 to 34, recording materials (vi-1) to (vi-9) have a crystal structure of a stoichiometric ternary compound having the respectively specified composition so that they have an increased rate of crystallization and improved stability in the amorphous phase thereof.

In recording materials (vi-1) to (vi-9), since at least one of the three constituent elements of the stoichiometric three-element compound is partly substituted by other element(s) to form a solid solution containing 4 or more kinds of elements, the stability of the amorphous phase of the recording material layer can further be improved.

Accordingly, the optical recording media using these recording materials are capable of not only conducting rewriting at a high speed but also maintaining the recorded information for a prolonged period of time.

Further, since recording materials (vi-1) to (vi-9) contain at least one of Se and Te and thus absorb visible to near infrared light, widespread light sources inclusive of semi-conductor lasers, can be utilized for recording.

In the cases when the constituent element(s) of the stoichiometric three-element compound which is-(are) to be substituted and the element(s) which substitute for the constituent element(s) are in the mutual relationship that they can form a full-range solid solution, the strain of crystal structure attended by the substitution is relatively small so that structural changes of the stoichiometric three-element compound due to the substitution can be minimized. Therefore, a permissible degree of substitution can be broadened to advantage.

In particular, where constituent element(s) of the stoichiometric three-element compound is-(are) partly substituted by Tl of the group III<sub>b</sub>, the resulting solid solution containing 4 or more kinds of elements has a furthermore increased rate of crystallization, thus increasing the rewriting speed.

### EXAMPLE 35

Optical recording media having a structure shown in Fig. 1 were prepared, each comprising 1.2 mm-thick acrylic resin substrate (1) having thereon 100 nm-thick inorganic dielectric material layer (2) made of SiO<sub>2</sub>, 100 nm-thick recording material layer (3) made of Sb-Te-Bi-Se, 100 nm-thick inorganic dielectric material layer (4) made of SiO<sub>2</sub>, ultraviolet curable acrylic resin adhesive layer (5), and 1.2 mm-thick acrylic resin protective layer (6) in this order.

Recording material layer (3) was formed by sputtering using an RF magnetron and two alloy targets, Sb<sub>2</sub>Te<sub>3</sub> (crystal structure: C33) and Bi<sub>2</sub>Se<sub>3</sub> (crystal structure C33) both belonging to the rhombohedral system, while appropriately controlling the RF power to the respective alloy target so as to synthesize a composition shown in Table 12 below.

Samples 77 and 78 showed absorption in the wavelength region of from visible light to near infrared light and could be used as optical recording media at least in the wavelength region of from 400 nm to 860 nm.

Recording and erasion characteristics when these recording media were used by using a semi-conductor laser having a wavelength of 830 nm as a light source are also shown in Table 12 below.

TABLE 12

Sample No.	Composition of Recording Material	Time of Crystallization	Stability
77	(Sb <sub>2</sub> Te <sub>3</sub> ) <sub>85</sub> (Bi <sub>2</sub> Se <sub>3</sub> ) <sub>15</sub>	good	good
78	(Sb <sub>2</sub> Te <sub>3</sub> ) <sub>60</sub> (Bi <sub>2</sub> Se <sub>3</sub> ) <sub>40</sub>	good	good

As is apparent from Table 12, Samples 77 and 78 according to the present invention have a reduced time of crystallization as compared with Sample 4 of Comparative Example 1, making it possible to conduct recording and erasion of information at a higher speed, and also have a higher crystallization temperature as compared with Sample 5 of Comparative Example 1, indicating improved stability of the amorphous phase.

The recording materials in these samples are composed of a mixture of Sb<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> both of which have not only the same crystal system (i.e., rhombohedral system) but the same crystal structure (i.e., C33). The strain in the crystal lattice was therefore extremely small with the free energy of the crystal phase being further reduced so that the time of crystallization required was especially short.

In addition, as expected from the pseudo-binary phase diagram shown in Fig. 34, the recording material

of Sample 77 is a congruent solid solution. As a result, the recording material suffers from no local crystallization during cooling while retaining the excellent characteristics even on repetition of rewriting.

5

EXAMPLE 36

Optical recording media (Samples 79 and 80) were prepared in the same manner as in Example 35, except that the recording material layer was composed of Sb-Se-Bi-S.

10 The Sb-Se-Bi-S recording material layer was formed by sputtering using a single target prepared by mixing  $\text{Sb}_2\text{Se}_3$  (crystal structure: D58) and  $\text{Bi}_2\text{S}_3$  (crystal structure: D58), both of which belong to the orthorhombic system, at a ratio of 84:16 (Sample 79) or 65:35 (Sample 80).

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

15

EXAMPLE 37

20 Optical recording media (Samples 81 and 82) were prepared in the same manner as in Example 35, except that the recording material layer was composed of In-Te-Tl-Se.

The In-Te-Tl-Se recording material layer was formed by sputtering using two alloy targets of InTe (crystal structure: B37) and TlSe (crystal structure: B37) both of which belong to the tetragonal system.

25 Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

EXAMPLE 38

30

A optical recording medium (Sample 83) was prepared in the same manner as in Example 35, except that the recording material layer was composed of Pb-Sn-Te.

The Pb-Sn-Te recording material layer was formed by simultaneous binary sputtering using two alloy targets of PbTe (crystal structure: B1) and SnTe (crystal structure: B1) both of which belong to the cubic system.

35 Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

40

EXAMPLE 39

A optical recording medium (Sample 84) was prepared in the same manner as in Example 35, except that the recording material layer was composed of In-Ga-Te.

45 The In-Ga-Te recording material layer was formed by simultaneous binary sputtering using two alloy targets of InSb (crystal structure: B3) and GaSb (crystal structure: B3) both of which belong to the cubic system.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

50

EXAMPLE 40

55 A optical recording medium (Sample 85) was prepared in the same manner as in Example 35, except that the recording material layer was composed of In-Ge-Te.

The In-Ge-Te recording material layer was formed by simultaneous binary sputtering using two alloy targets of  $\text{In}_2\text{Te}_3$  (crystal structure: B3) and GeTe (crystal structure: B1) both of which belong to the cubic

system.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

5

#### EXAMPLE 41

A optical recording medium (Sample 86) was prepared in the same manner as in Example 35, except that the recording material layer was composed of Sb-Ge-Se.

The Sb-Ge-Se recording material layer was formed by simultaneous binary sputtering using two alloy targets of  $\text{Sb}_2\text{Se}_3$  (crystal structure: D58) and GeSe (crystal structure: B29) both of which belong to the orthorombic system.

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

15

#### EXAMPLE 42

20

A optical recording medium (Sample 87) was prepared in the same manner as in Example 35, except that the recording material layer was composed of Bi-Te-S-Se.

The Bi-Te-S-Se recording material layer was formed by simultaneous binary sputtering using two alloy targets of  $\text{Bi}_2\text{Te}_2\text{S}$  (crystal structure: C33) and  $\text{Bi}_2\text{Se}_3$  (crystal structure: C33) both of which belong to the rhombohedral system.

25

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

30

#### EXAMPLE 43

A optical recording medium (Sample 88) was prepared in the same manner as in Example 35, except that the recording material layer was composed of Sb-Te-Bi-Se.

The Sb-Te-Bi-Se recording material layer was formed by simultaneous ternary sputtering using three alloy targets of  $\text{Sb}_2\text{Te}_3$  (crystal structure: C33),  $\text{Bi}_2\text{Te}_3$  (crystal structure: C33), and  $\text{Bi}_2\text{Se}_3$  (crystal structure: C33) all of which belong to the rhombohedral system.

35

Recording and erasion characteristics of the resulting optical recording media are shown in Table 13 below.

40

TABLE 13

45

50

55

Example No.	Sample No.	Composition of Recording Material	Time of Crystallization	Stability
36	79	$(\text{Sb}_2\text{Se}_3)_{84}(\text{Bi}_2\text{S}_3)_{16}$	good	good
"	80	$(\text{Sb}_2\text{Se}_3)_{65}(\text{Bi}_2\text{S}_3)_{35}$	good	good
37	81	$(\text{InTe})_{52}(\text{TlSe})_{48}$	good	good
"	82	$(\text{InTe})_{80}(\text{TlSe})_{20}$	good	good
38	83	$(\text{PbTe})_{30}(\text{SnTe})_{70}$	good	good
39	84	$(\text{InSb})_{80}(\text{GaSb})_{20}$	good	good
40	85	$(\text{In}_2\text{Te}_3)_{95}(\text{GeTe})_5$	good	good
41	86	$(\text{Sb}_2\text{Se}_3)_{95}(\text{GeSe})_5$	good	good
42	87	$(\text{Bi}_2\text{Te}_2\text{S})_{25}(\text{Bi}_2\text{Se}_3)_{75}$	good	good
43	88	$(\text{Sb}_2\text{Te}_3)_{85}(\text{Bi}_2\text{Te}_3)_{10}(\text{Bi}_2\text{Se}_3)_5$	good	good

As is apparent from Table 13, Samples 79 to 88 according to the present invention have a reduced time

of crystallization, making it possible to conduct recording and erasion of information at a higher speed, and also have a higher crystallization temperature, an indication of improved stability of the amorphous phase, as compared with Comparative Example 1, similarly to Samples 77 to 78 of Example 35.

In particular, the recording materials in Examples 35 to 39 and 42 to 43 were those synthesized from a mixture of stoichiometric compounds which are the same not only in crystal system but in crystal structure. As a result, the strain in the crystal lattice in these materials is extremely small to further reduce the free energy of the crystal phase, to thereby achieve marked reduction in crystallization time.

Since each of the recording materials of Samples 79 and 81 is composed of a congruent solid solution as expected from the respective pseudo-binary phase diagram shown in Fig. 35 or 36, they suffer from no local crystallization during cooling and retain satisfactory characteristics even on repetition of rewriting.

It is apparent from Examples 35 to 43 that use of recording material (vii) according to the present invention increases stability of the recording material layer in its amorphous phase and reduces the time of crystallization of the recording material layer. The optical recording media using recording material (vii) are thus capable of rewriting at a high speed and maintaining recorded information for an extended period of time.

Because recording material (vii) shows absorption of visible and near infrared light due to the presence of at least one of Se and Te, widespread light sources inclusive of semi-conductor lasers can be applied to these materials.

Where the above-described elements or stoichiometric compounds having the same crystal system also have the same crystal structure according to classification by strukturbericht, the recording material composed of such elements or stoichiometric compounds has an extremely small strain in its crystal lattice, and the free energy of the crystal phase is further reduced, which leads to further reduction of the crystallization time.

In addition, where the solid solution constituting recording material (vii) is a congruent solid solution, local crystallization does not take place during cooling so that unchangeability of the recording characteristics on repeated use is further ensured.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

30

Amendments		
Page	line	
35	2	12 et seq.
	2	22 et seq.
	3	17
	17	2 et seq.
	60	20 et seq.
40	60	22 et seq.
	63	20
	86	3-4
	90	11
	93	20
45	106	9

(throughout the specification): "change" instead of "transition"  
 (throughout the specification): "erasing" instead of "erasion"  
 "Ge-Se-Te" instead of "Ge-St-Te"  
 (throughout the specification): "crystalline phase" instead of "crystal phase"  
 (throughout the specification): "co-sputtering" instead of "simultaneous sputtering"  
 (throughout the specification): "power" instead of "voltage"  
 "segregation" instead of "local crystallization"  
 "widespread light sources inclusive of" to be deleted  
 "partly" instead of "partlyr"  
 "recording" instead of "rewriting"  
 "recording and erasing characteristics" instead of "recording characteristics"

## 50 Claims

1. An optical recording medium comprising a substrate having provided thereon a layer of a recording material whose optical properties reversibly change on application of light or heat, to conduct recording, reproduction, or erasion of information, wherein said recording material is:

(i) a recording material having a composition corresponding to a mixture of (i-a) a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element selected from Sn and Pb and the  $VI_b$  group element selected from S, Se, and Te and represented by chemical formula  $IV_bVI_b$  and (i-b) a  $V_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element selected from Sb, Bi, and As and the group

VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula V<sub>b2</sub>VI<sub>b3</sub>, said composition containing at least one of Se and Te.

(ii) a recording material having a composition corresponding to a mixture of (ii-a) a congruent compound having a composition corresponding to a mixture of (ii-a-1) a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Sn and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b</sub> and (ii-a-2) a V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group V<sub>b</sub> element selected from Sb, Bi, and As and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula V<sub>b2</sub>VI<sub>b3</sub> and (ii-b) the above-described V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound, said composition containing at least one of Se and Te.

(iii) a recording material having a composition corresponding to a mixture of (iii-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (iii-b) a stoichiometric compound composed of elements selected from at least two groups of the group III<sub>b</sub> consisting of Ga, In, and Tl, the group IV<sub>b</sub> consisting of Ge, Sn, and Pb, the group V<sub>b</sub> consisting of As, Sb, and Bi, and the group VI<sub>b</sub> consisting of S, Se, and Te, said composition containing at least one of Se and Te.

(iv) a recording material having a composition corresponding to a mixture of (iv-a) a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub> and (iv-b) a stoichiometric compound composed of elements selected from at least two groups of the group III<sub>b</sub> consisting of Ga, In, and Tl, the group IV<sub>b</sub> consisting of Ge, Sn, and Pb, the group V<sub>b</sub> consisting of As, Sb, and Bi, and the group VI<sub>b</sub> consisting of S, Se, and Te, said composition containing 3 or more kinds of elements and containing at least one of Se and Te.

(v) a recording material having a composition corresponding to a mixture of (v-a) a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub> and (v-b) a stoichiometric compound composed of elements selected from at least two groups of the group III<sub>b</sub> consisting of Ga, In, and Tl, the group IV<sub>b</sub> consisting of Ge, Sn, and Pb, and the group VI<sub>b</sub> consisting of S, Se, and Te, said composition containing 3 or more kinds of elements and containing at least one of Se and Te.

(vi-1) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-1-a) a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Sn and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b2</sub> and (vi-1-b) a V<sub>b</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group V<sub>b</sub> element selected from Sb, Bi, and As and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula V<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of said stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups IV<sub>b</sub>, V<sub>b</sub>, and VI<sub>b</sub> and Si and Ge of the group IV<sub>b</sub>.

(vi-2) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-2-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag, and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (vi-2-b) a V<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group V<sub>b</sub> element selected from As, Sb, and Bi and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula V<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of said stoichiometric three-element compound is partly substituted by at least one element selected from the above-described elements of the groups I, V<sub>b</sub>, and VI<sub>b</sub>.

(vi-3) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-3-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (vi-3-b) a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of said stoichiometric three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups I, III<sub>b</sub>, and VI<sub>b</sub> and Al of

the group III<sub>b</sub>.

(vi-4) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-4-a) a I<sub>2</sub>VI<sub>b</sub> type stoichiometric compound composed of the group I element selected from Li, Na, K, Rb, Cs, Cu, Ag and Au and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula I<sub>2</sub>VI<sub>b</sub> and (vi-4-b) a IV<sub>b</sub>VI<sub>b2</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b2</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups I, IV<sub>b</sub>, and VI<sub>b</sub> and Si of the group IV<sub>b</sub>.

(vi-5) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-5-a) a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub> and (vi-5-b) a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub>, IV<sub>b</sub>, and VI<sub>b</sub>, Al of the group III<sub>b</sub>, and Si of the group IV<sub>b</sub>.

(vi-6) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-6-a) a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub> and (vi-6-b) a IV<sub>b</sub>VI<sub>b2</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b2</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub>, IV<sub>b</sub> and VI<sub>b</sub>, Al of the group III<sub>b</sub>, and Si of the group IV<sub>b</sub>.

(vi-7) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of two kinds of a III<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b</sub>VI<sub>b</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub> and VI<sub>b</sub> and Al of the group III<sub>b</sub>.

(vi-8) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of two kinds of a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub> and VI<sub>b</sub> and Al of the group III<sub>b</sub>.

(vi-9) a recording material made of a solid solution containing 4 or more kinds of elements at least one of which is Se or Te and having a crystal structure of a stoichiometric three-element compound having a composition corresponding to a mixture of (vi-9-a) a III<sub>b2</sub>VI<sub>b3</sub> type stoichiometric compound composed of the group III<sub>b</sub> element selected from Ga, In, and Tl and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula III<sub>b2</sub>VI<sub>b3</sub> and (vi-9-b) a IV<sub>b</sub>VI<sub>b</sub> type stoichiometric compound composed of the group IV<sub>b</sub> element selected from Ge, Sn, and Pb and the group VI<sub>b</sub> element selected from S, Se, and Te and represented by chemical formula IV<sub>b</sub>VI<sub>b</sub>, in which at least one of the three constituent elements of said three-element compound is partly substituted by at least one element selected from the group consisting of the above-described elements of the groups III<sub>b</sub>, IV<sub>b</sub>, and VI<sub>b</sub>, Al of the group III<sub>b</sub>, and Si of the group IV<sub>b</sub>, and

(vii) a recording material made of a solid solution composed of at least three elements selected from the group consisting of the group III<sub>b</sub> element selected from Ga, In, and Tl, the group IV<sub>b</sub> element selected from Ge, Sn, and Pb, the group V<sub>b</sub> element selected from As, Sb, and Bi, and the group VI<sub>b</sub> element selected from S, Se, and Te and containing at least one of Se and Te, said solid solution being synthesized

from plural elements or stoichiometric compounds having the same crystal system.

2. An optical recording medium as claimed in Claim 1, wherein said recording is the recording material (i).
3. An optical recording medium as claimed in Claim 1, wherein said recording is the recording material (ii).
4. An optical recording medium as claimed in Claim 2, wherein the crystal phase of said recording material (i) is a single phase composed of a stoichiometric compound.
5. An optical recording medium as claimed in Claim 3, wherein the crystal phase of said recording material (ii) is a single phase composed of a stoichiometric compound.
6. An optical recording medium as claimed in Claim 4, wherein said stoichiometric compound is a congruent compound.
7. An optical recording medium as claimed in Claim 5, wherein said stoichiometric compound is a congruent compound.
8. An optical recording medium as claimed in Claim 2, wherein said recording material (i) is a single phase composed of a solid solution.
9. An optical recording medium as claimed in Claim 3, wherein said recording material (ii) is a single phase composed of a solid solution.
10. An optical recording medium as claimed in Claim 1, wherein said recording is the recording material (iii).
11. An optical recording medium as claimed in Claim 10, wherein said stoichiometric compound (iii-b) is a  $V_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $V_b$  element and the group  $VI_b$  element and represented by chemical formula of  $V_{b2}VI_{b3}$ .
12. An optical recording medium as claimed in Claim 10, wherein said multiple stoichiometric compound (iii-b) is a  $III_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $III_b$  element and the group  $VI_b$  element and represented by chemical formula of  $III_{b2}VI_{b3}$ .
13. An optical recording medium as claimed in Claim 10, wherein said multiple stoichiometric compound (iii-b) is a  $IV_bVI_{b2}$  type stoichiometric compound composed of the group  $IV_b$  element and the group  $VI_b$  element and represented by chemical formula of  $IV_bVI_{b2}$ .
14. An optical recording medium as claimed in Claim 10, wherein the crystal phase of said recording material (iii) is a single phase composed of a stoichiometric compound.
15. An optical recording medium as claimed in Claim 14, wherein said stoichiometric compound is a congruent compound.
16. An optical recording medium as claimed in Claim 10, wherein said recording material is a single phase composed of a solid solution.
17. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (iv).
18. An optical recording medium as claimed in Claim 17, wherein said stoichiometric compound (iv-b) is a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element and the group  $VI_b$  element and represented by chemical formula of  $IV_bVI_b$ .
19. An optical recording medium as claimed in Claim 17, wherein said stoichiometric compound (iv-b) is a  $IV_bVI_{b2}$  type stoichiometric compound composed of the group  $IV_b$  element and the group  $VI_b$  element and represented by chemical formula of  $IV_bVI_{b2}$ .
20. An optical recording medium as claimed in Claim 17, wherein said stoichiometric compound (iv-b) is a  $III_bVI_b$  type stoichiometric compound composed of the group  $III_b$  element and the group  $VI_b$  element and represented by chemical formula of  $III_bVI_b$ .
21. An optical recording medium as claimed in Claim 1, wherein said recording is the recording material (v).
22. An optical recording medium as claimed in Claim 21, wherein said stoichiometric compound (v-b) is a  $III_{b2}VI_{b3}$  type stoichiometric compound composed of the group  $III_b$  element and the group  $VI_b$  element and represented by chemical formula of  $III_{b2}VI_{b3}$ .
23. An optical recording medium as claimed in Claim 21, wherein said stoichiometric compound (v-b) is a  $IV_bVI_b$  type stoichiometric compound composed of the group  $IV_b$  element and the group  $VI_b$  element and represented by chemical formula of  $IV_bVI_b$ .
24. An optical recording medium as claimed in Claim 17, wherein the crystal phase of the recording material is a single phase composed of a stoichiometric compound.
25. An optical recording medium as claimed in Claim 21, wherein the crystal phase of the recording material is a single phase composed of a stoichiometric compound.
26. An optical recording medium as claimed in Claim 24, wherein said stoichiometric compound is a



congruent compound.

27. An optical recording medium as claimed in Claim 25, wherein said stoichiometric compound is a congruent compound.

28. An optical recording medium as claimed in Claim 17, wherein said recording material is a single phase composed of a solid solution.

29. An optical recording medium as claimed in Claim 21, wherein said recording material is a single phase composed of a solid solution.

30. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-1).

31. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-2).

32. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-3).

33. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-4).

34. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-5).

35. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-6).

36. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-7).

37. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-8).

38. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vi-9).

39. An optical recording medium as claimed in Claim 30, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

40. An optical recording medium as claimed in Claim 31, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

41. An optical recording medium as claimed in Claim 32, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

42. An optical recording medium as claimed in Claim 33, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

43. An optical recording medium as claimed in Claim 34, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

44. An optical recording medium as claimed in Claim 35, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

45. An optical recording medium as claimed in Claim 36, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

46. An optical recording medium as claimed in Claim 37, wherein at least one of the three constituent elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

47. An optical recording medium as claimed in Claim 38, wherein at least one of the three constituent

elements of said stoichiometric three-element compound which is partly substituted and at least one element which substitutes for said constituent element(s) are in the mutual relationship that they can form a solid solution regardless of the mixing ratio of the former element to the latter element.

5 48. An optical recording medium as claimed in Claim 32, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

49. An optical recording medium as claimed in Claim 34, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

10 50. An optical recording medium as claimed in Claim 35, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

51. An optical recording medium as claimed in Claim 36, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

15 52. An optical recording medium as claimed in Claim 37, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

53. An optical recording medium as claimed in Claim 38, wherein at least one element which substitutes for at least one of the three constituent elements of said stoichiometric three-element compound is Tl of the group III<sub>b</sub>.

54. An optical recording medium as claimed in Claim 1, wherein said recording material is the recording material (vii).

25 55. An optical recording medium as claimed in Claim 54, wherein said elements or stoichiometric compounds having the same crystal system have the same crystal structure according to the classification by strukturbericht.

56. An optical recording medium as claimed in Claim 54, wherein said solid solution is a congruent solid solution.

30 57. An optical recording medium as claimed in Claim 55, wherein said solid solution is a congruent solid solution.

35

40

45

50

55

Fig. 1

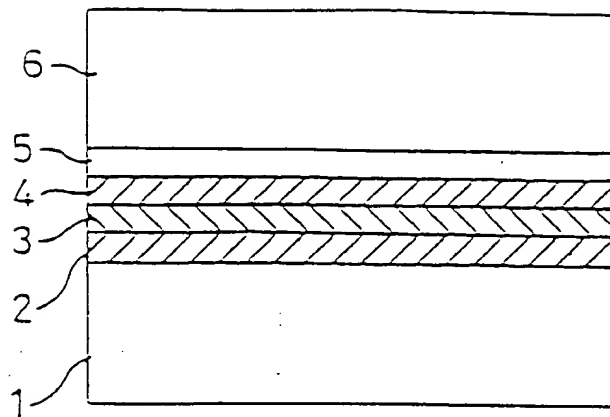


Fig. 2

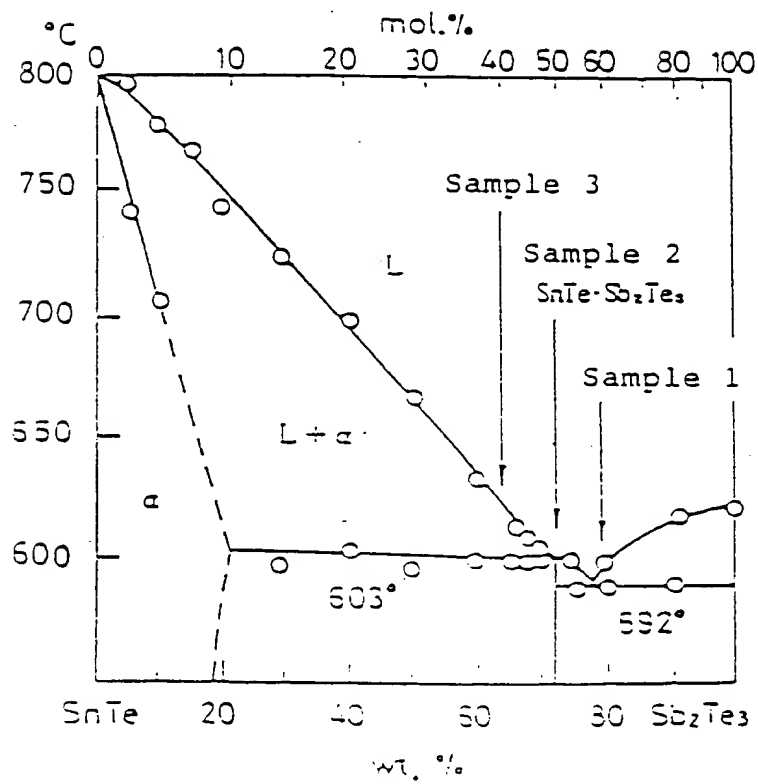


Fig. 3

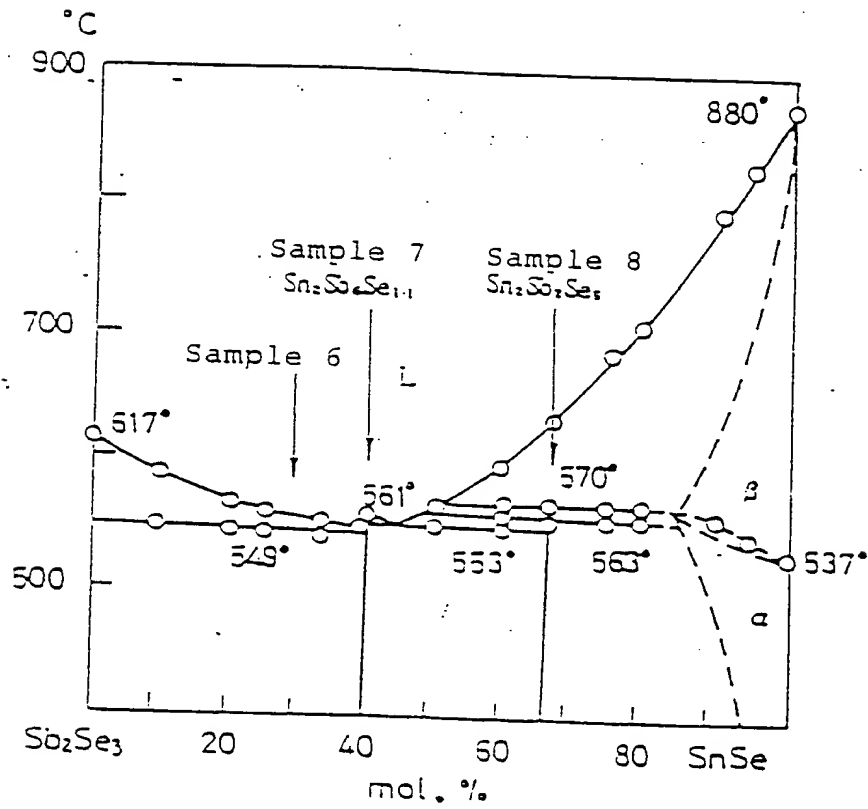


Fig. 4

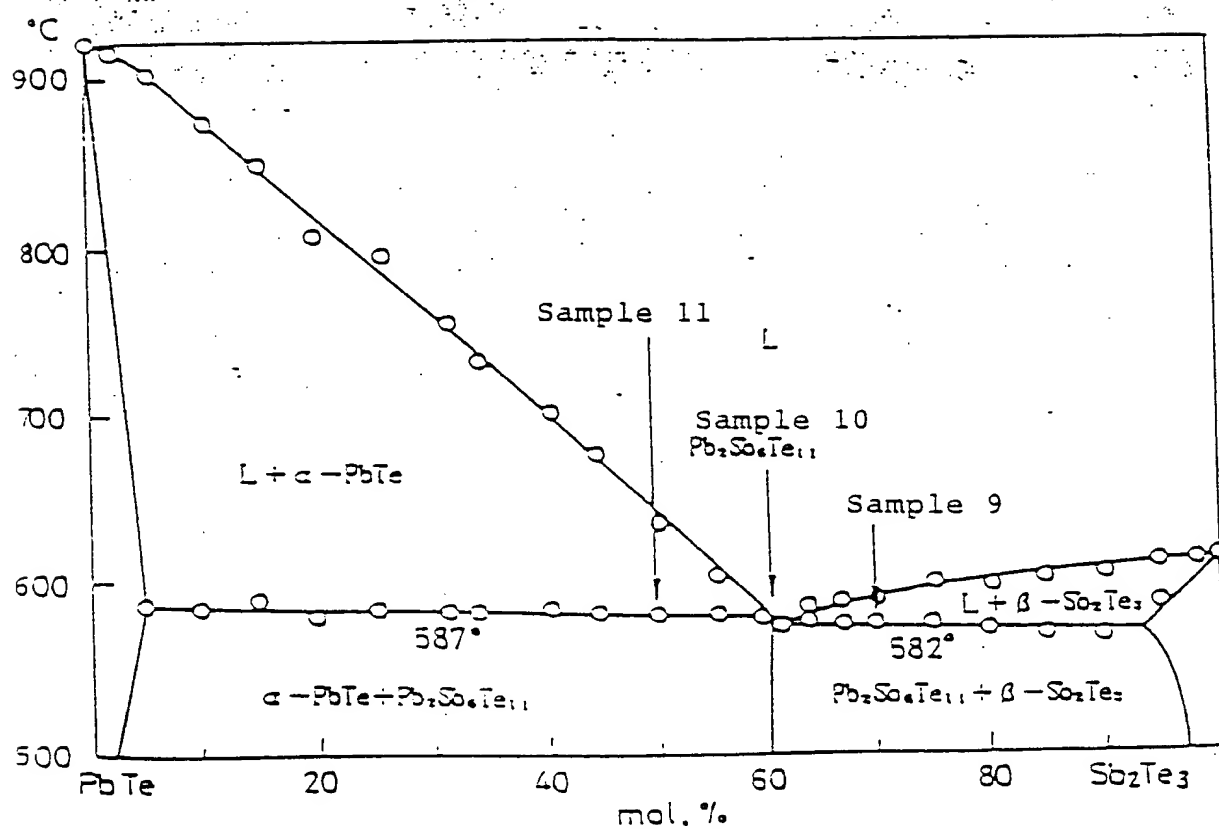


Fig. 5

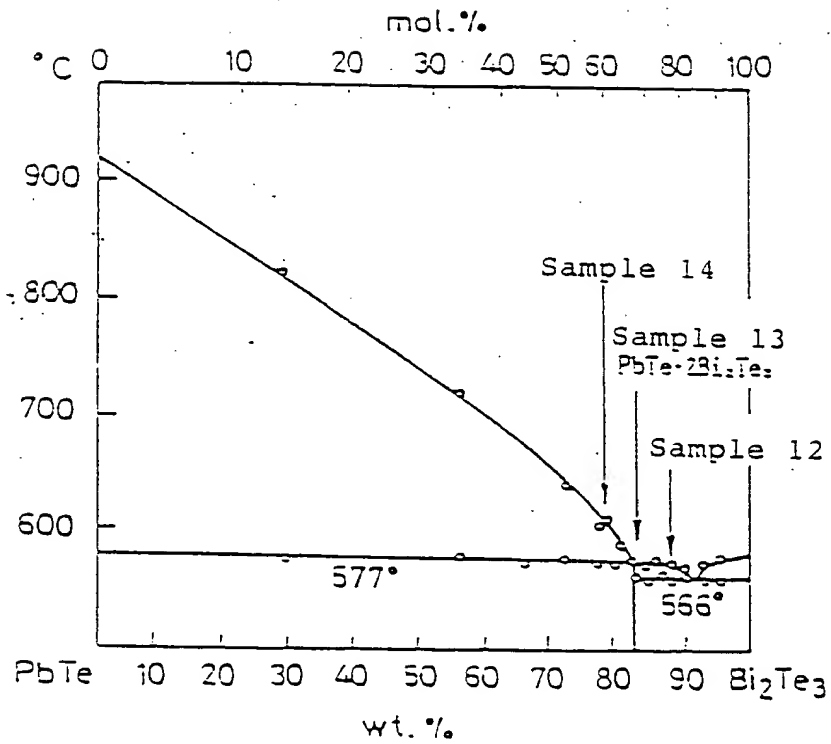


Fig. 6

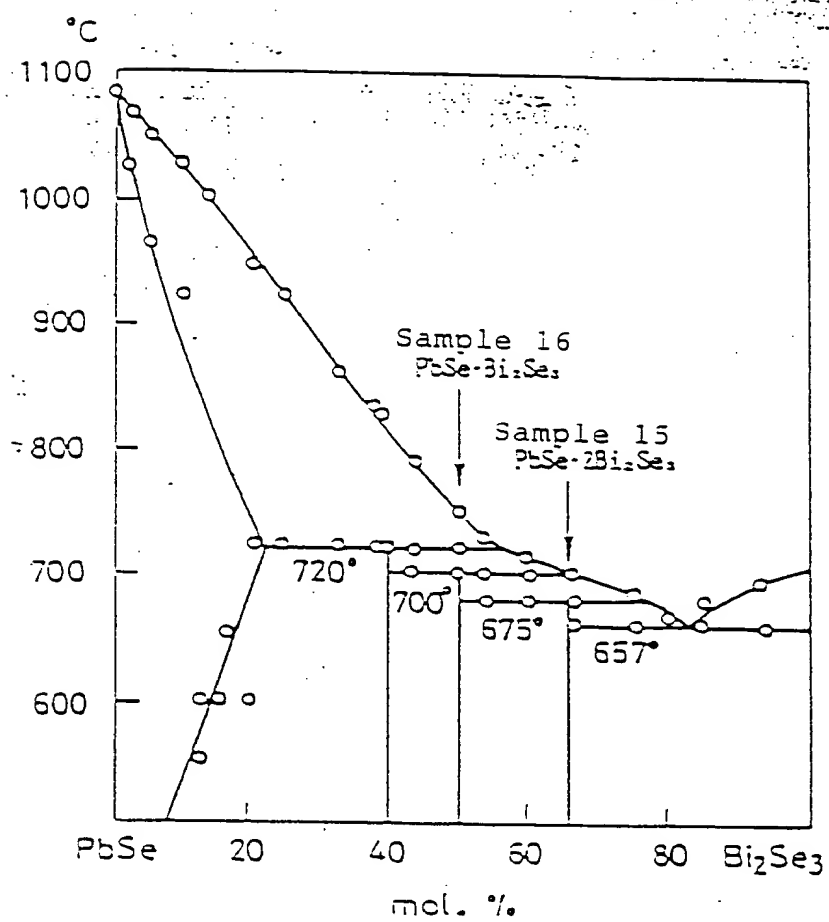


Fig. 7

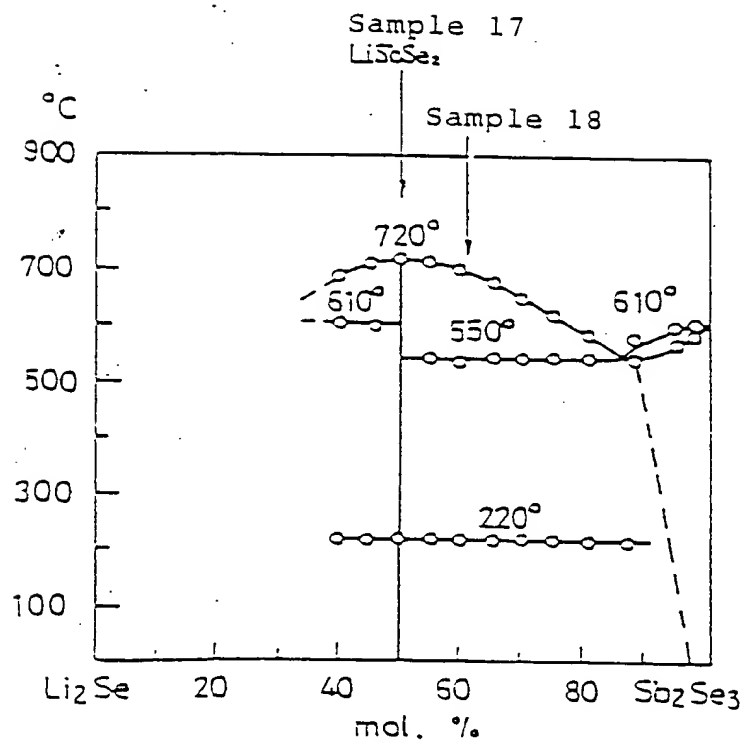




Fig. 8

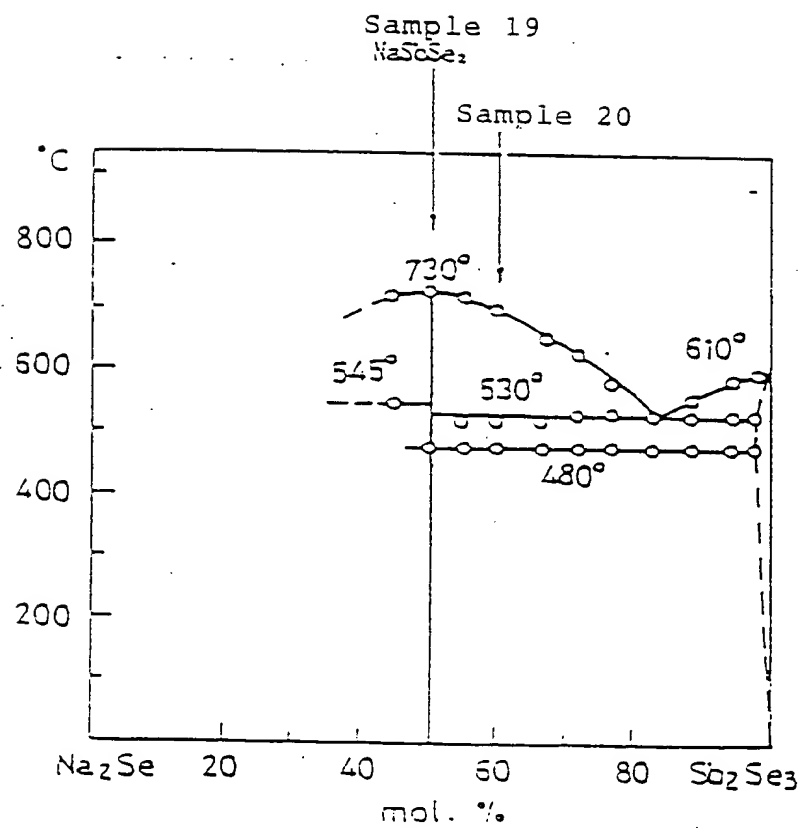
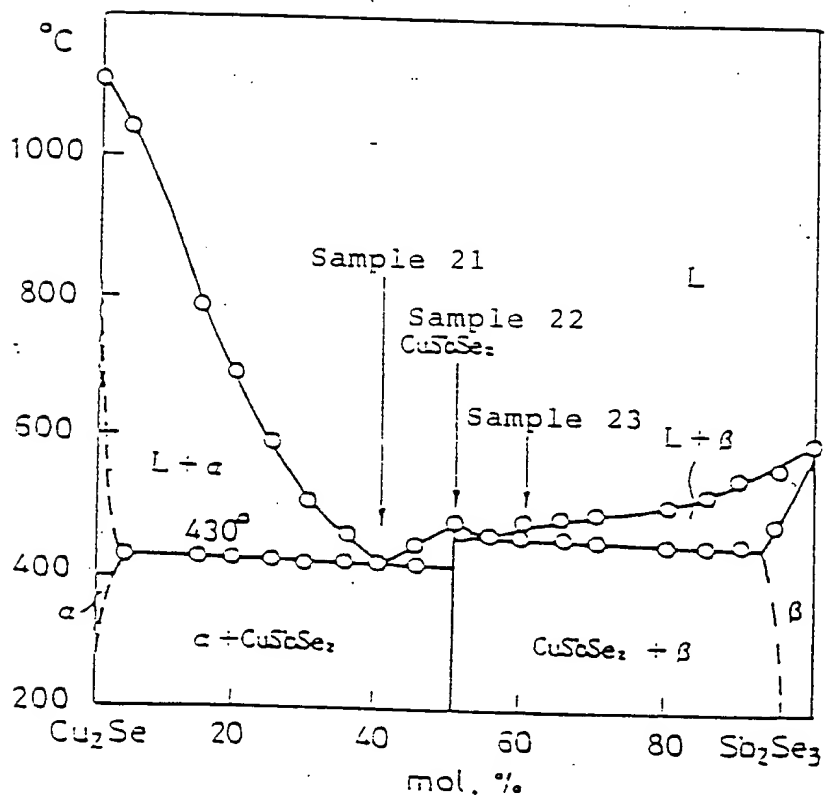
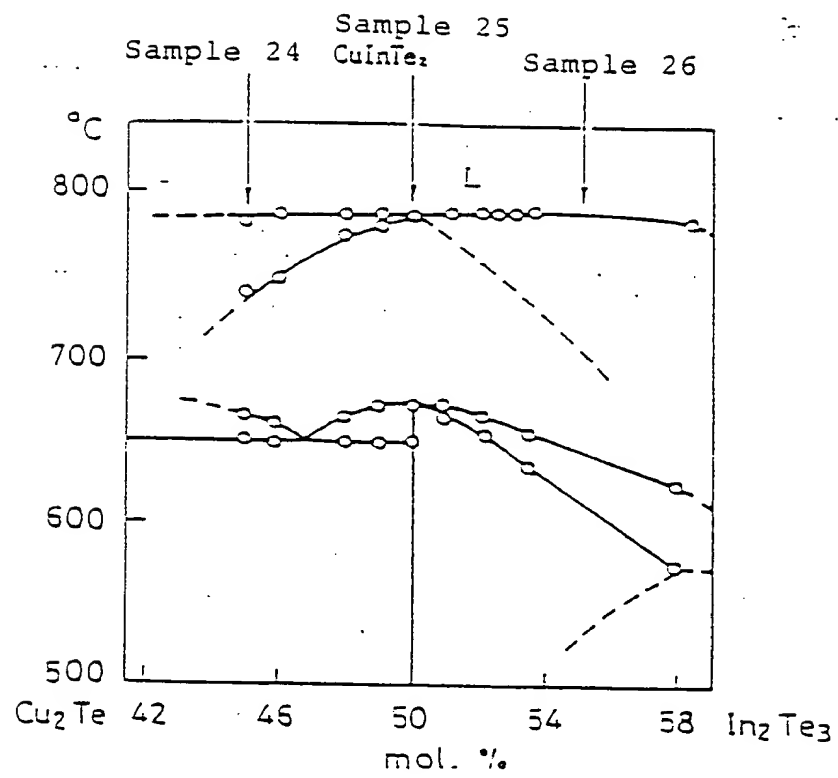


Fig. 9



Fi. 10



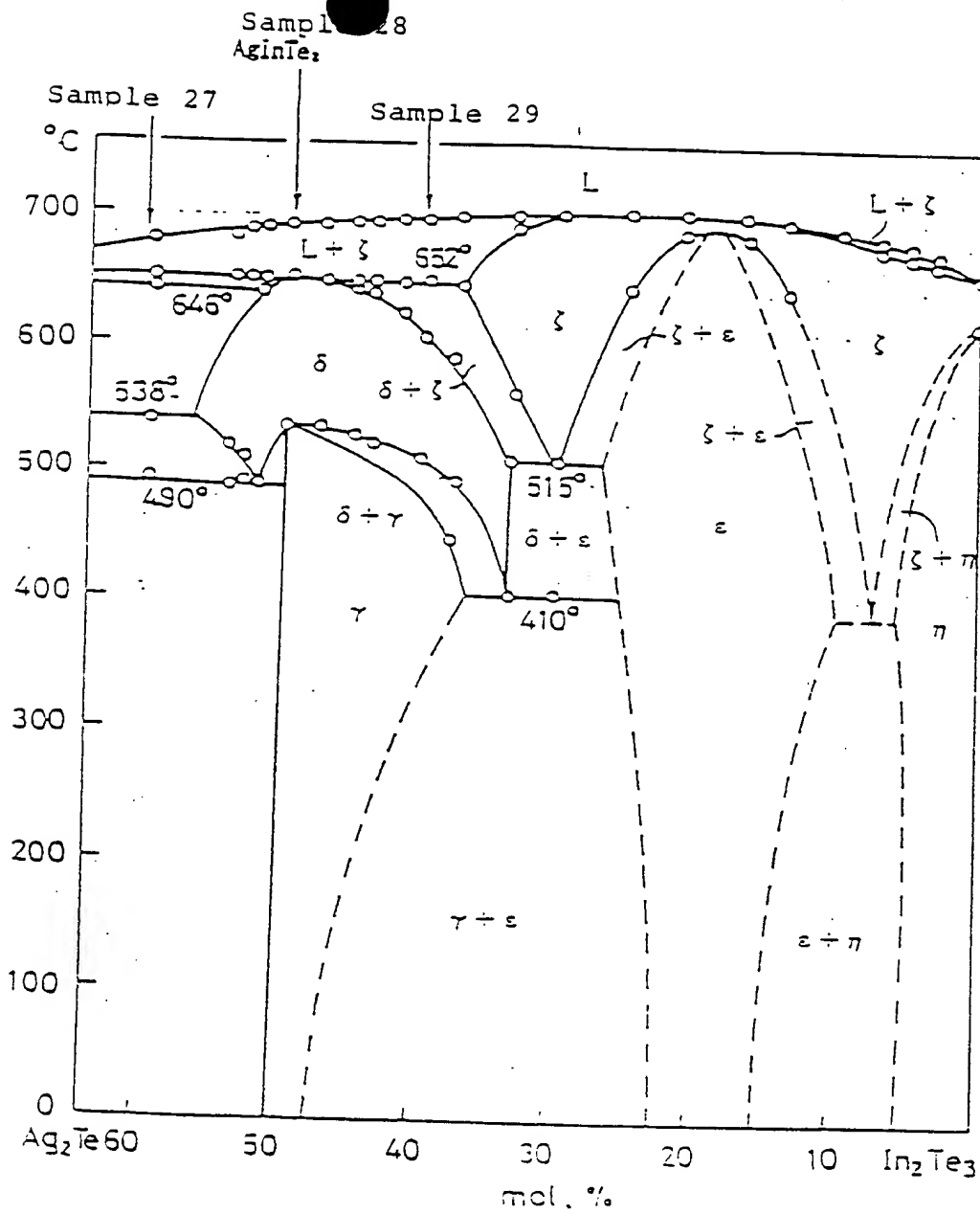


Fig. 12

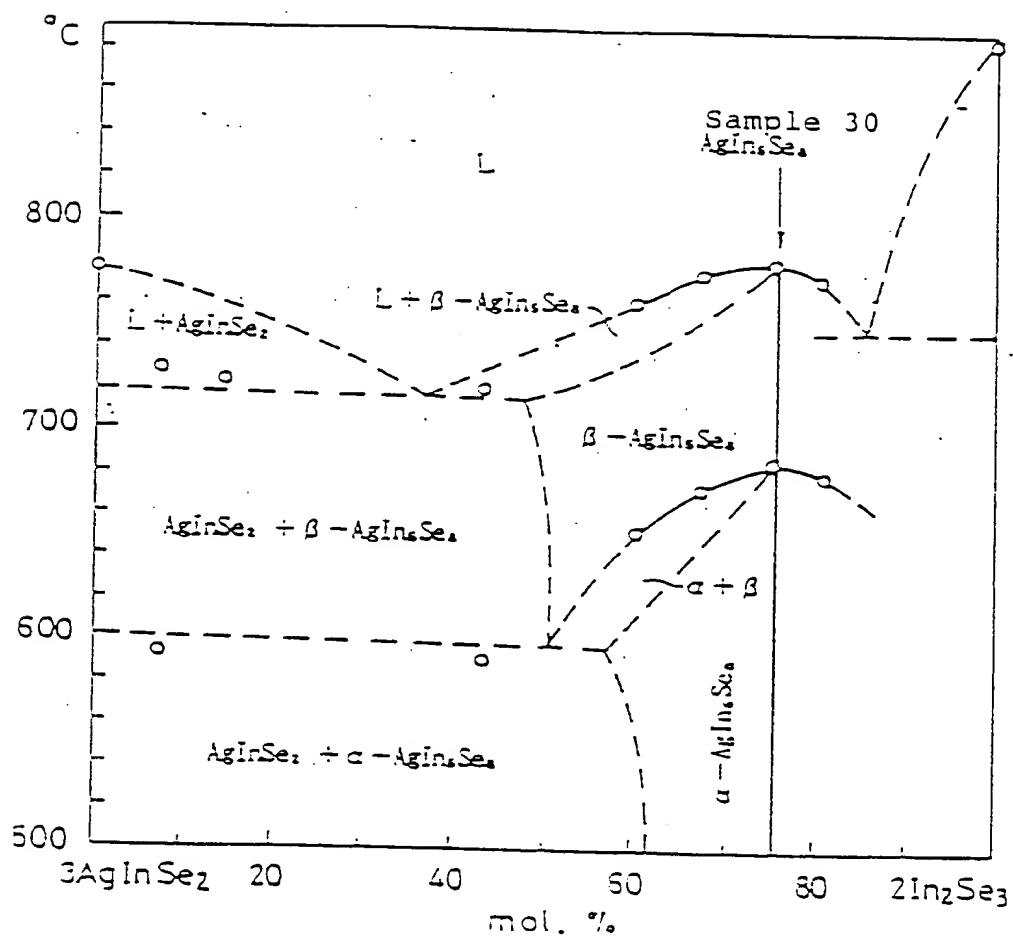


Fig. 13

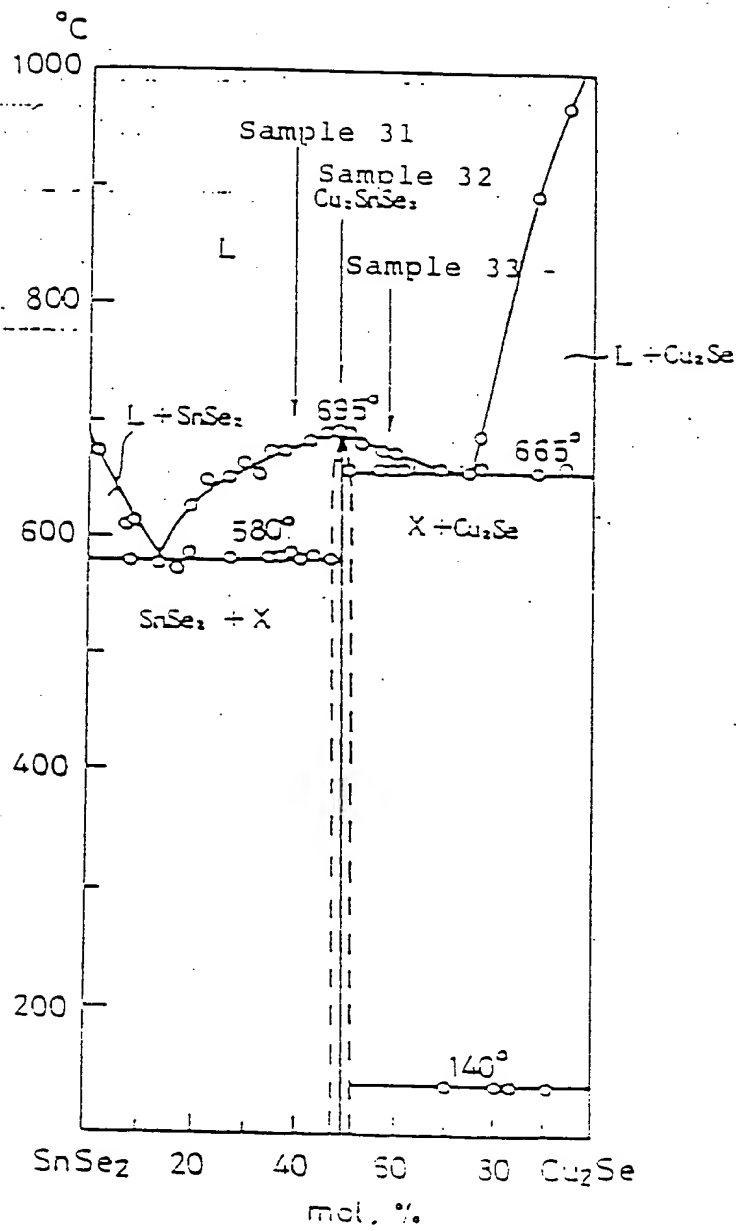


Fig. 14

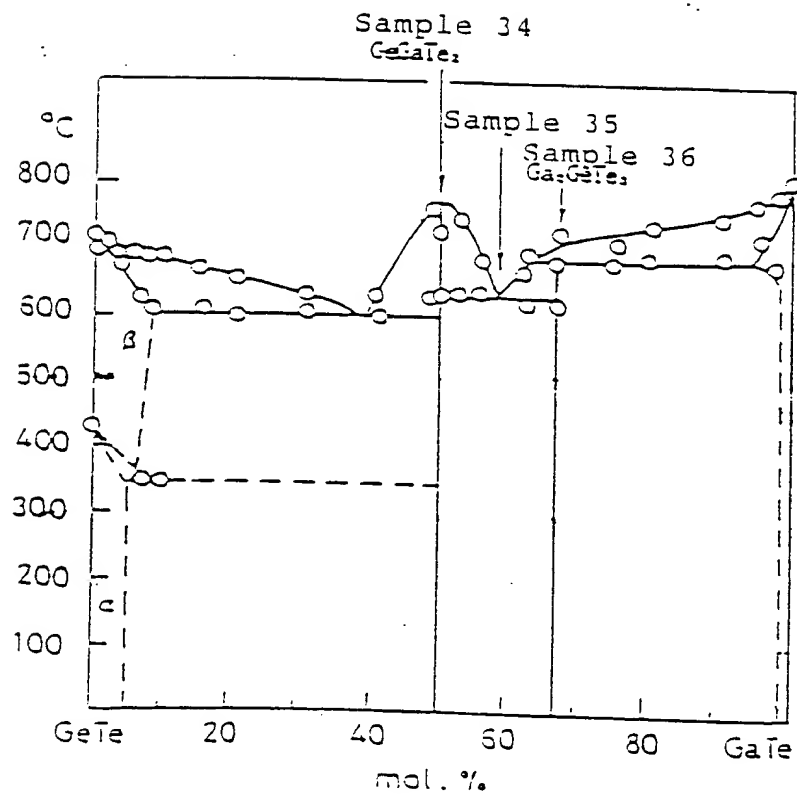
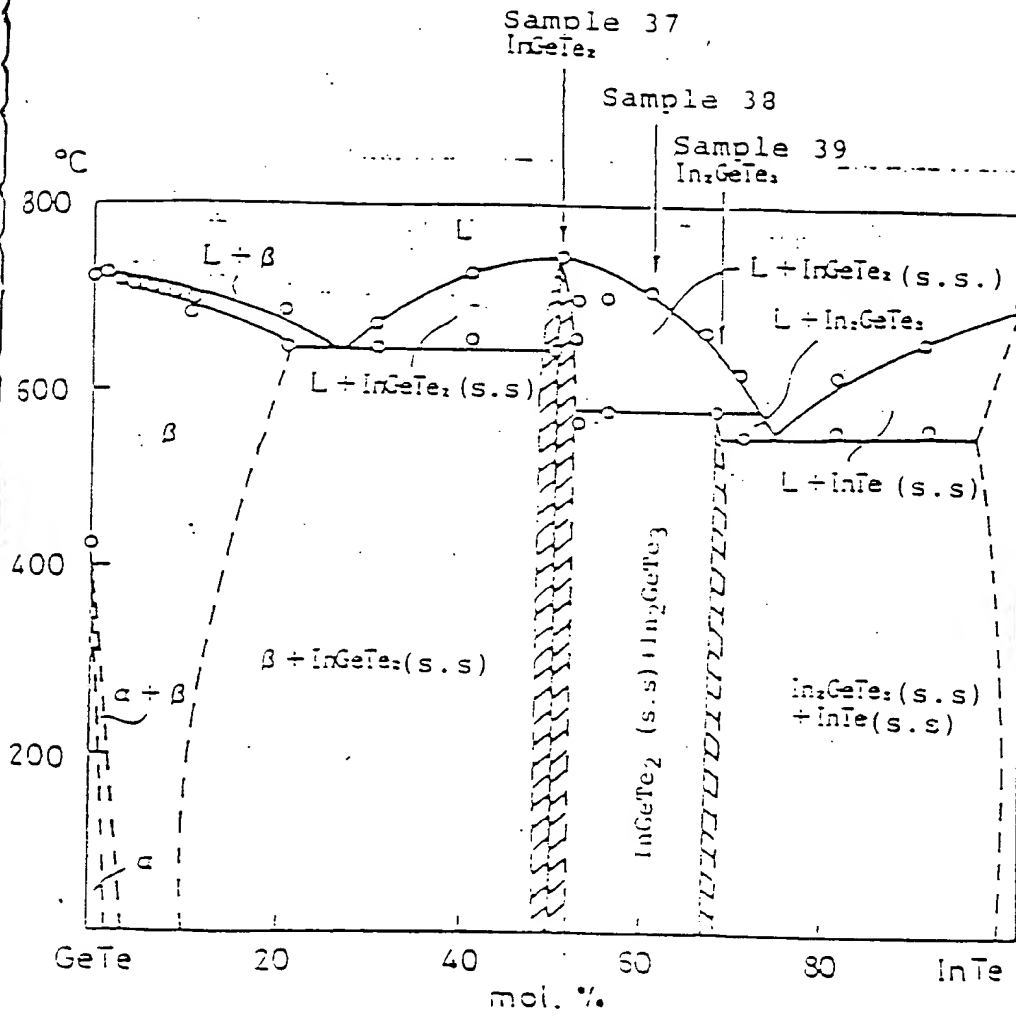


Fig. 15



(s.s. : solid solution)



Fig. 16

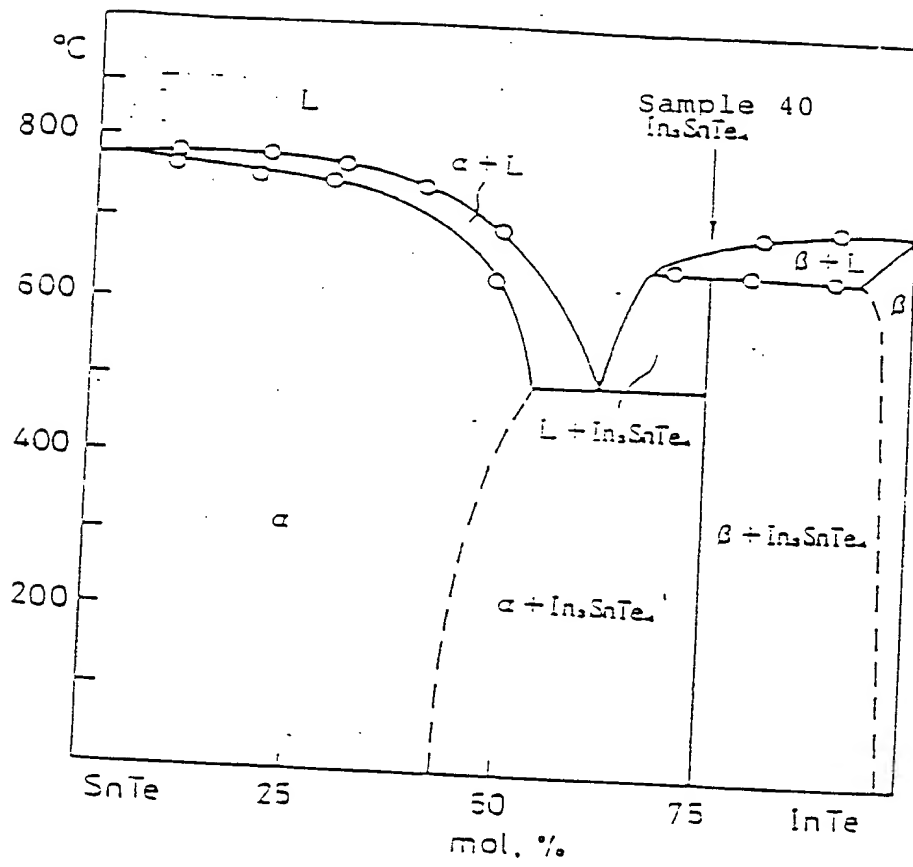


Fig. 17

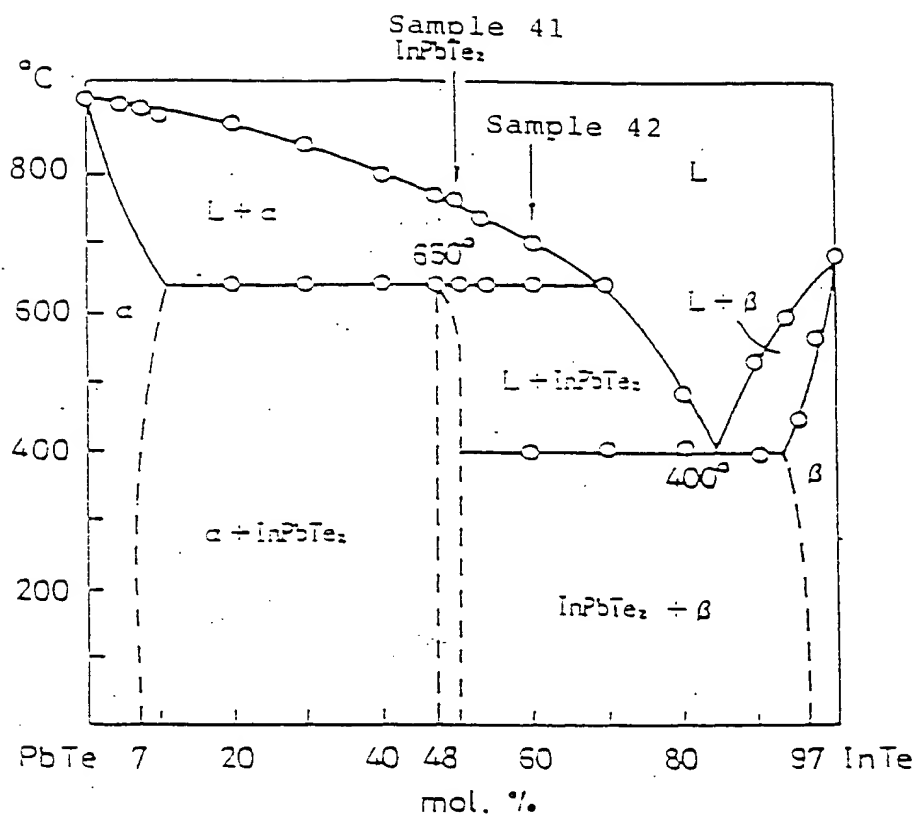


Fig. 18

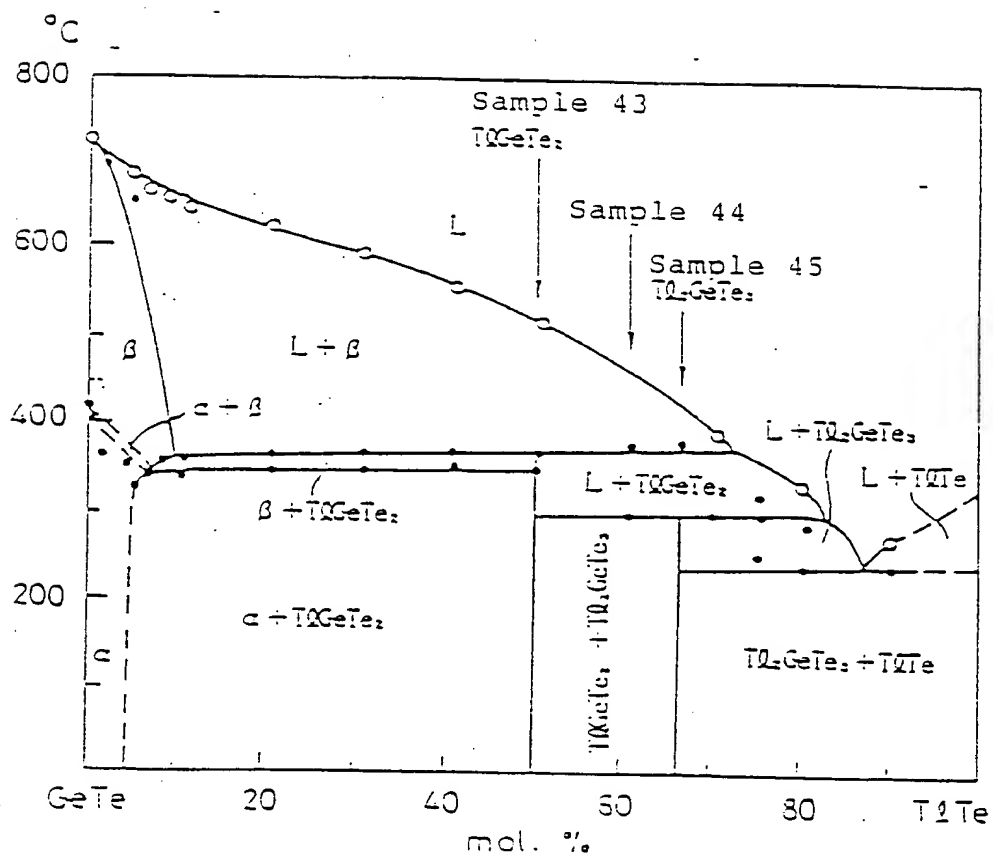


Fig. 19

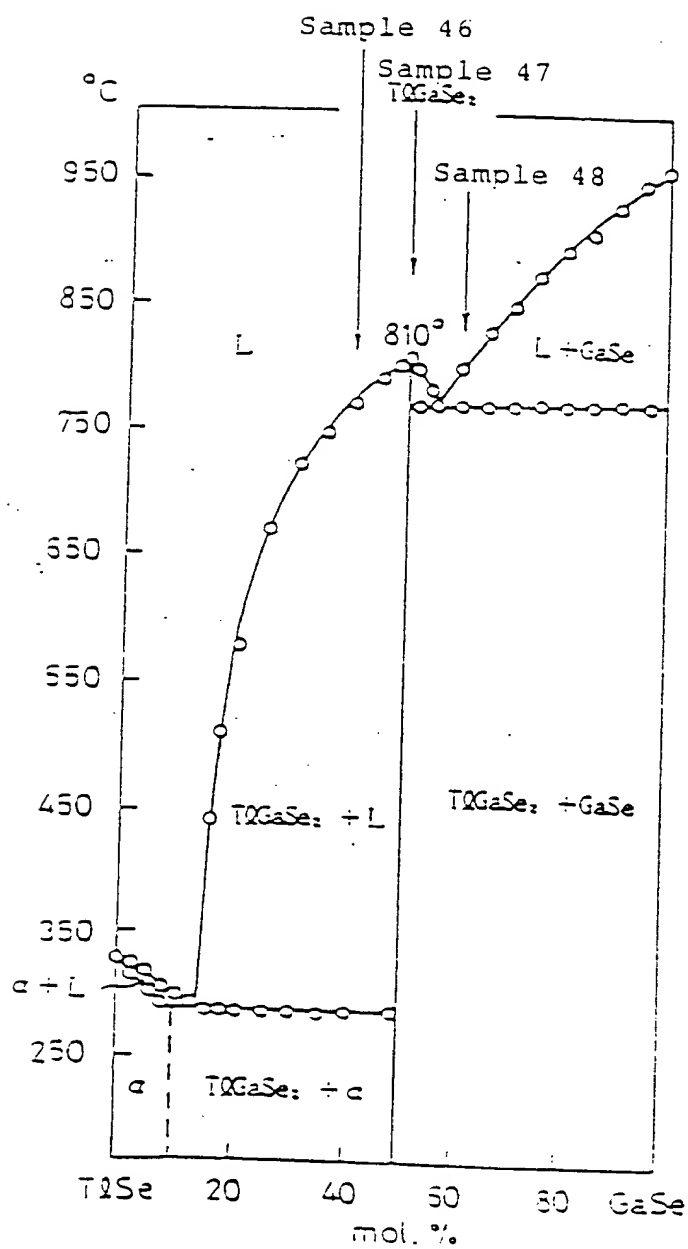


Fig. 20

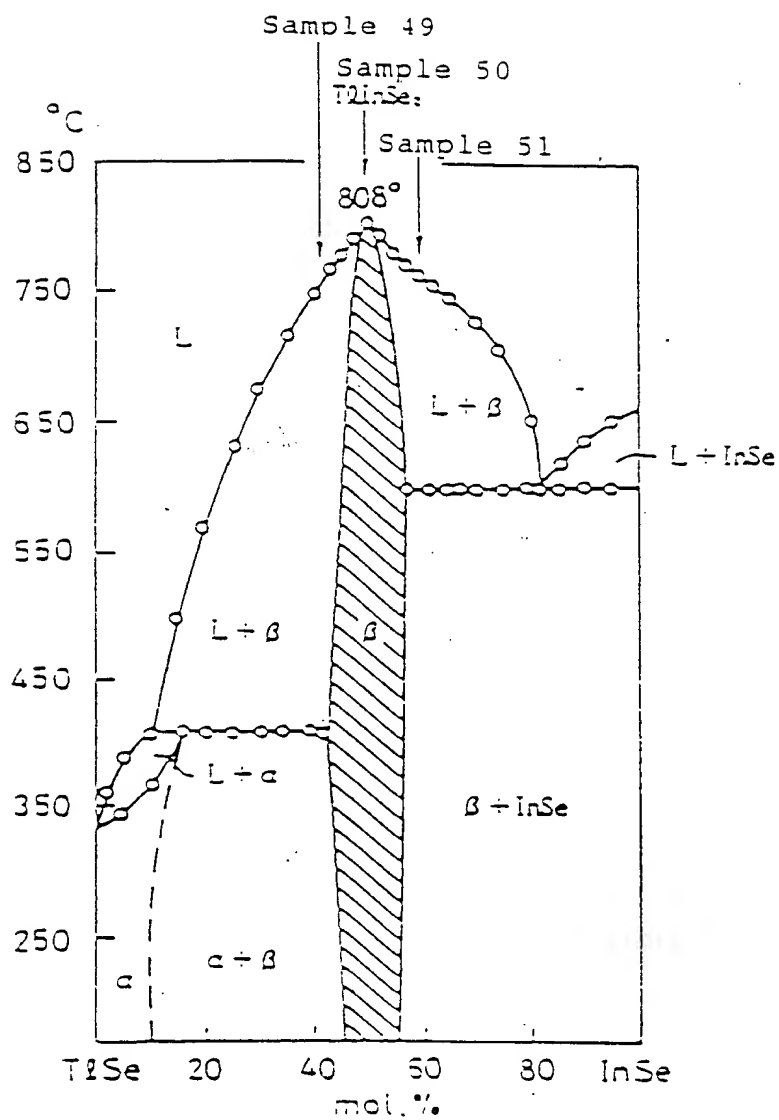


Fig. 21

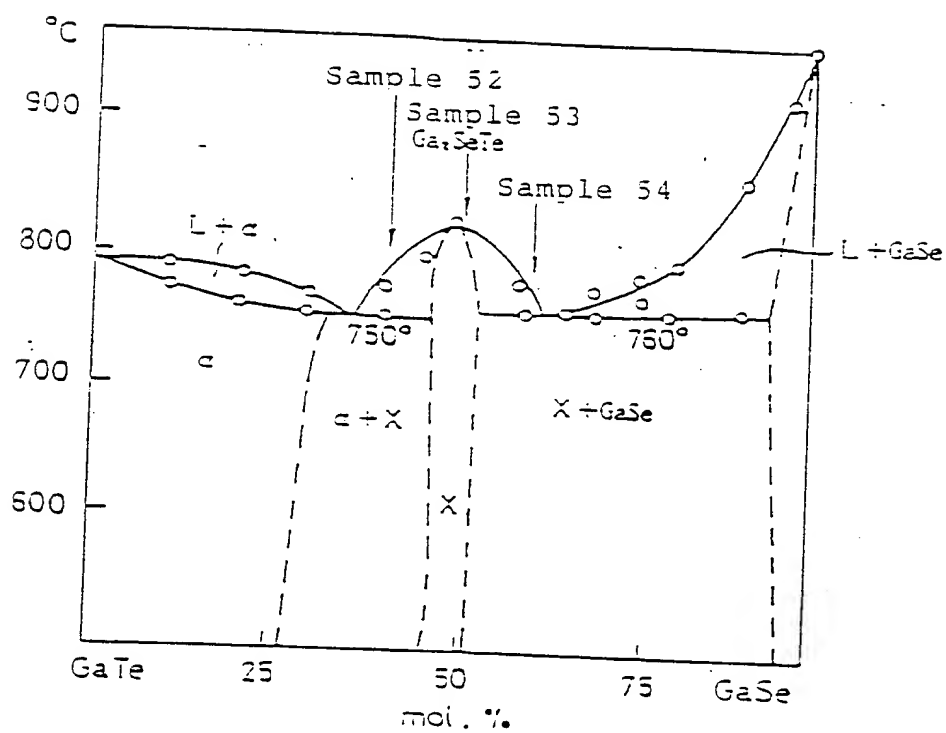


Fig. 22

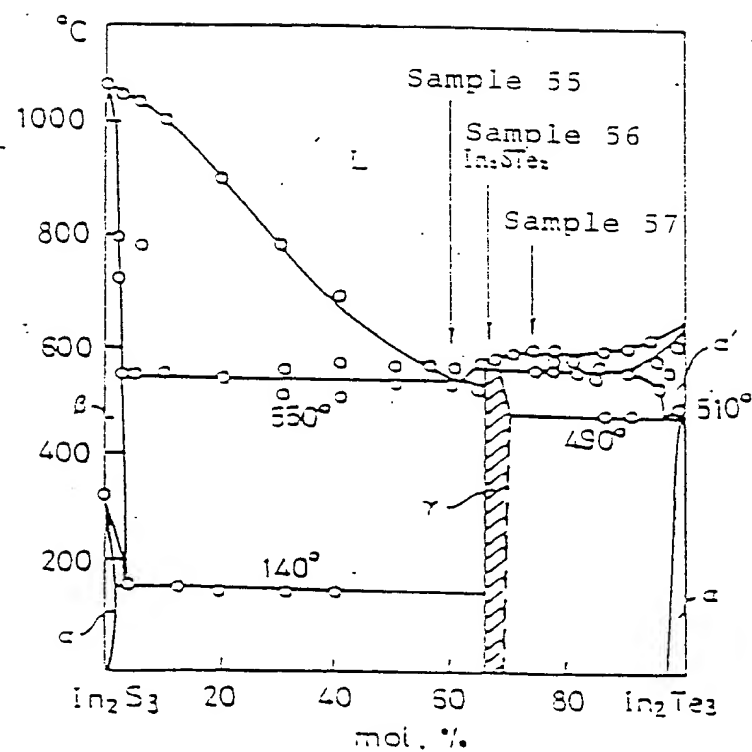


Fig. 23

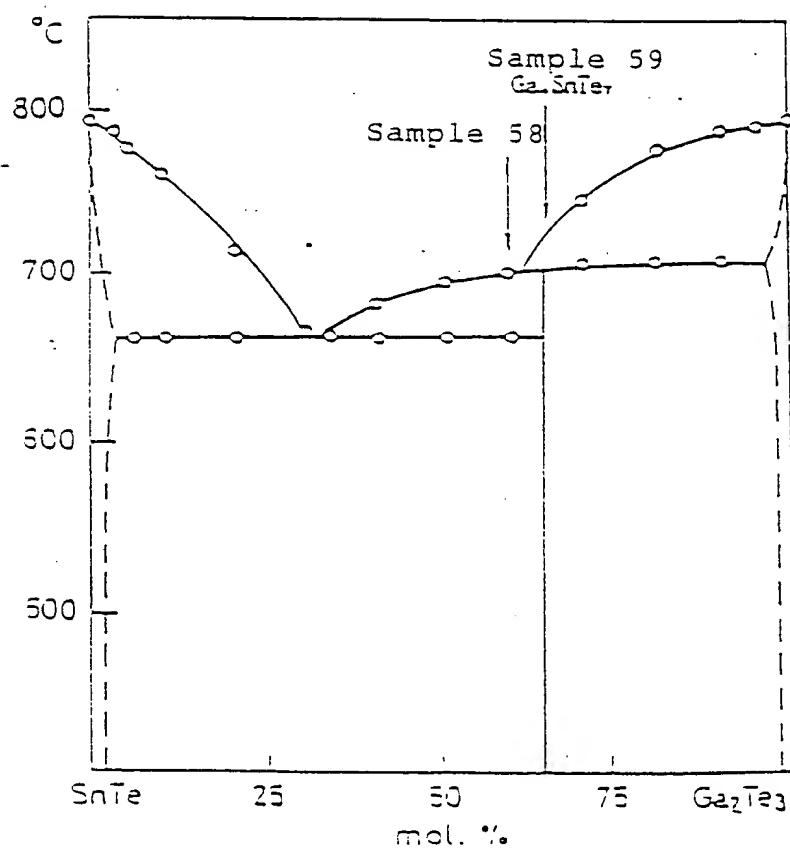




Fig. 24

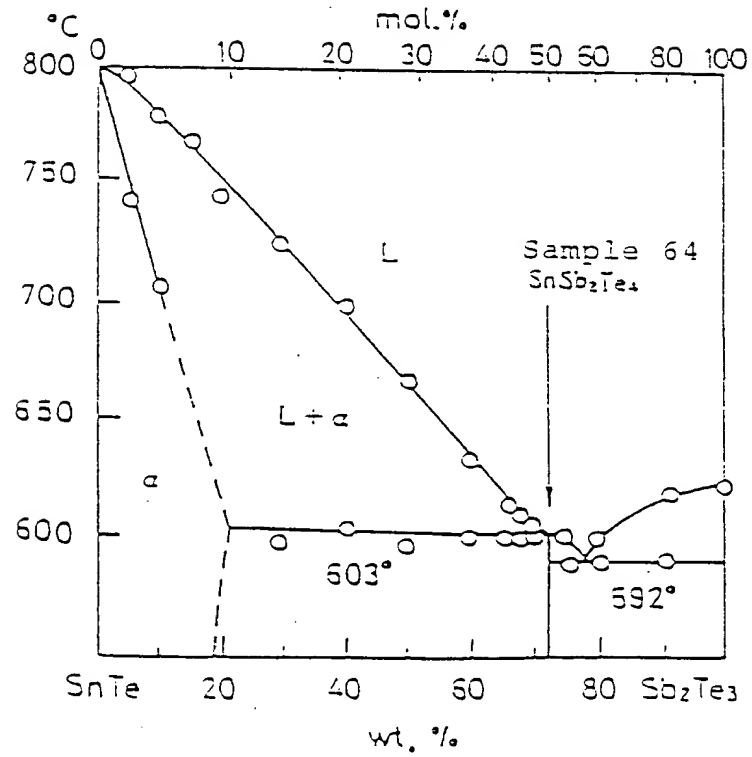


Fig. 25

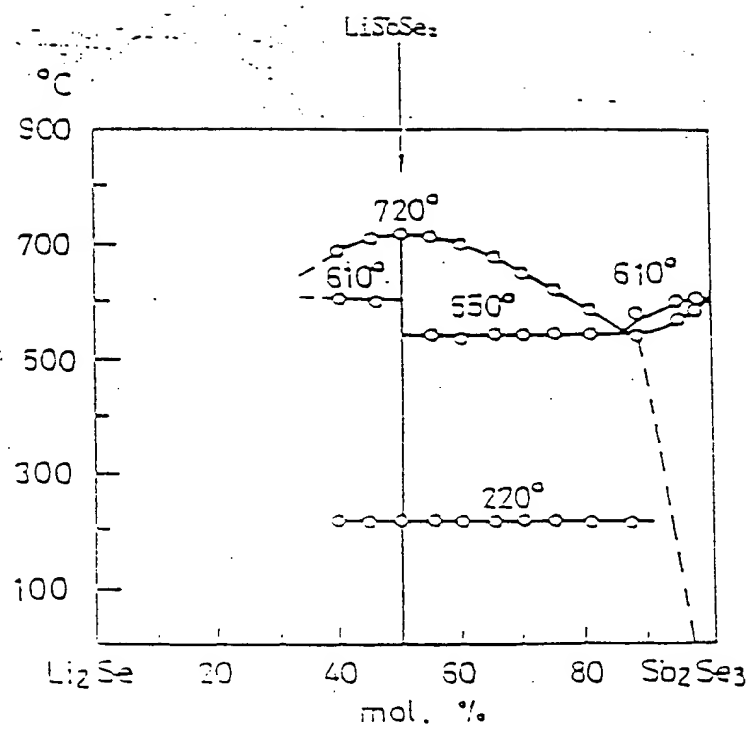


Fig. 26

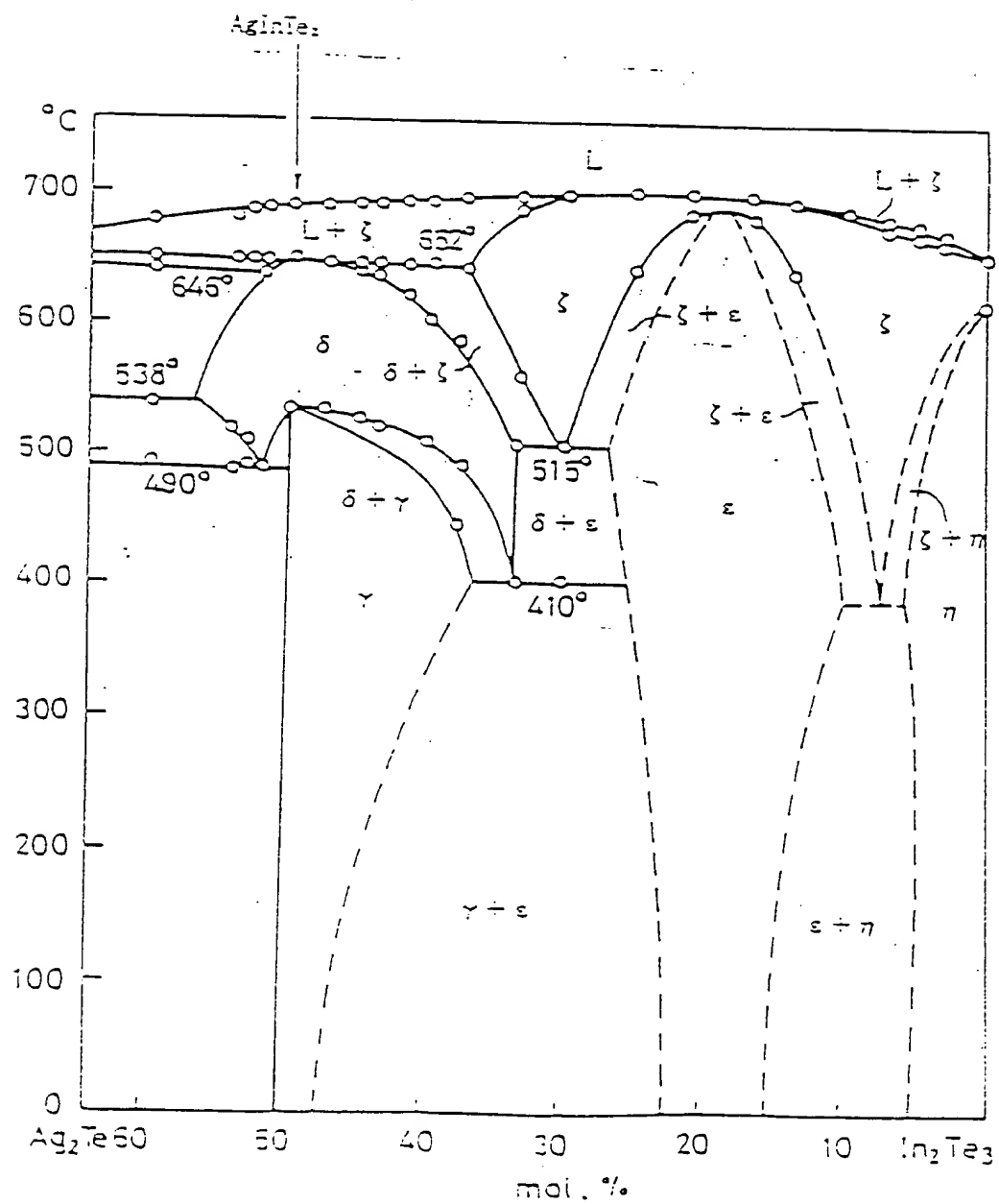


Fig. 27

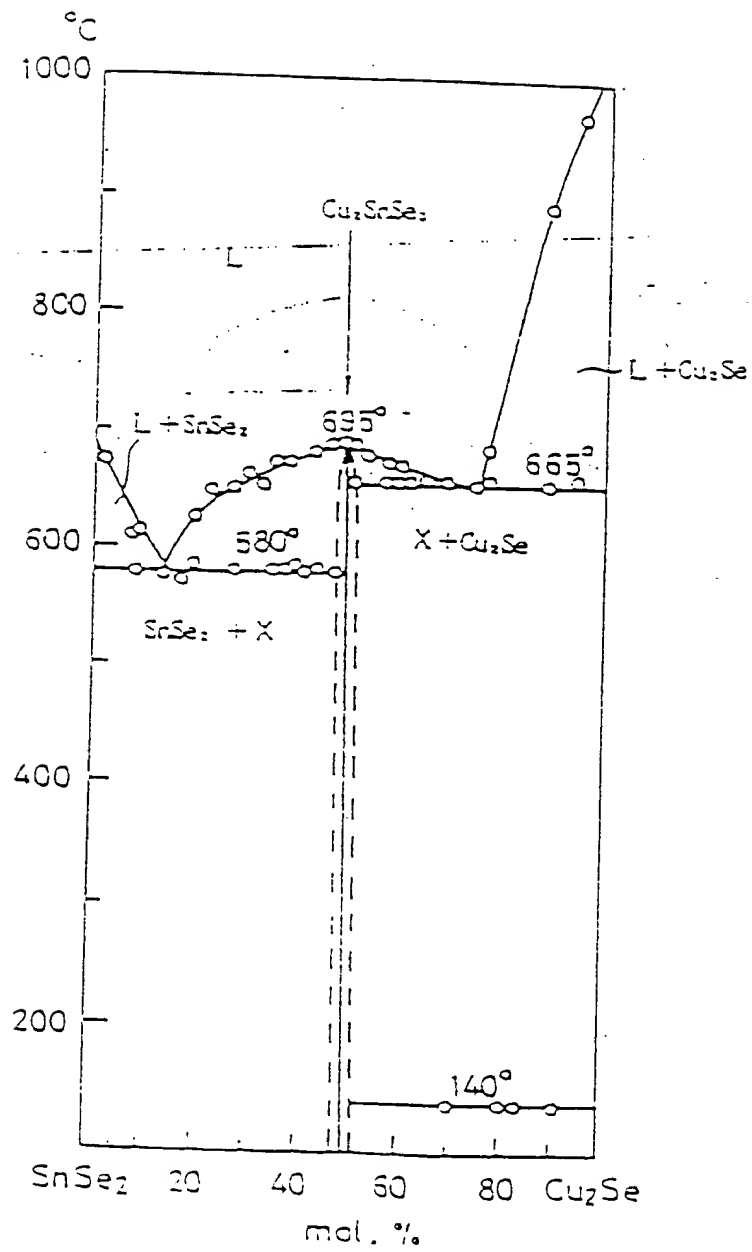
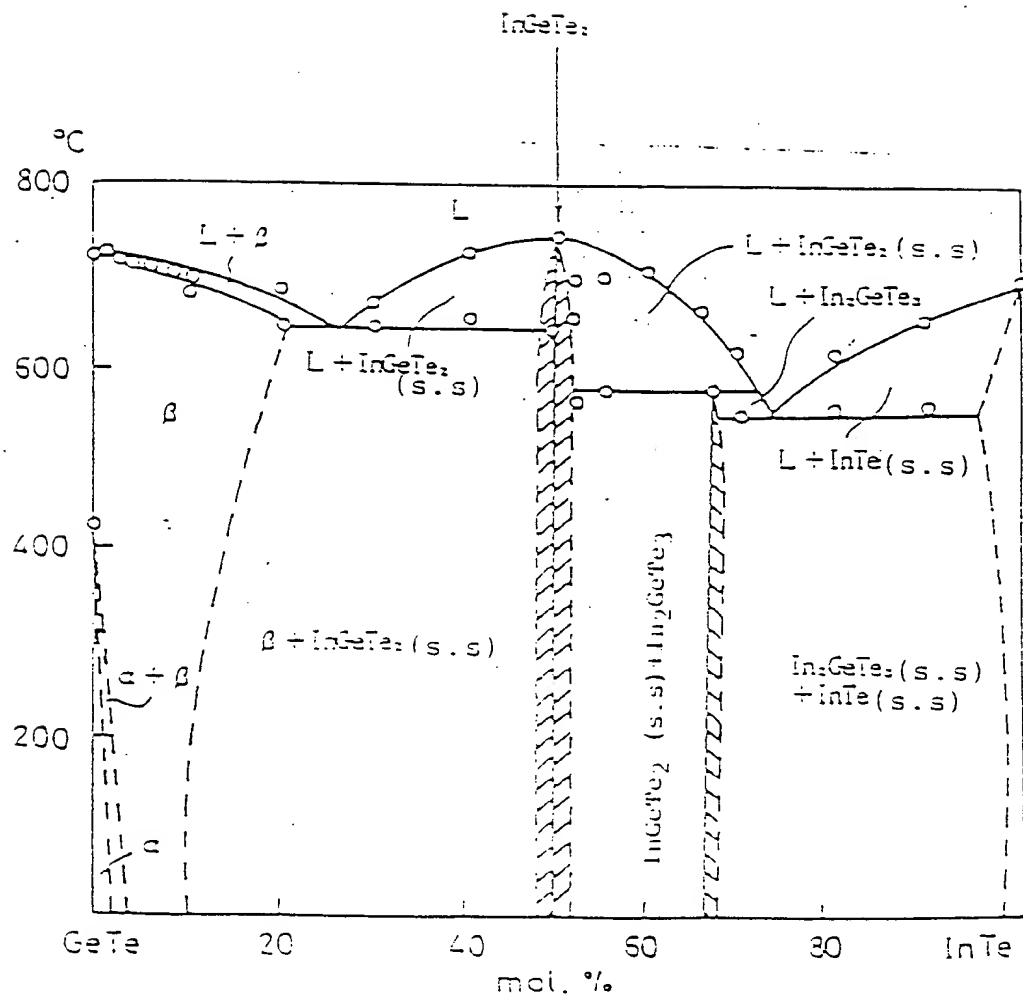


Fig. 23



(s.s. : solid solution)

Fig. 29

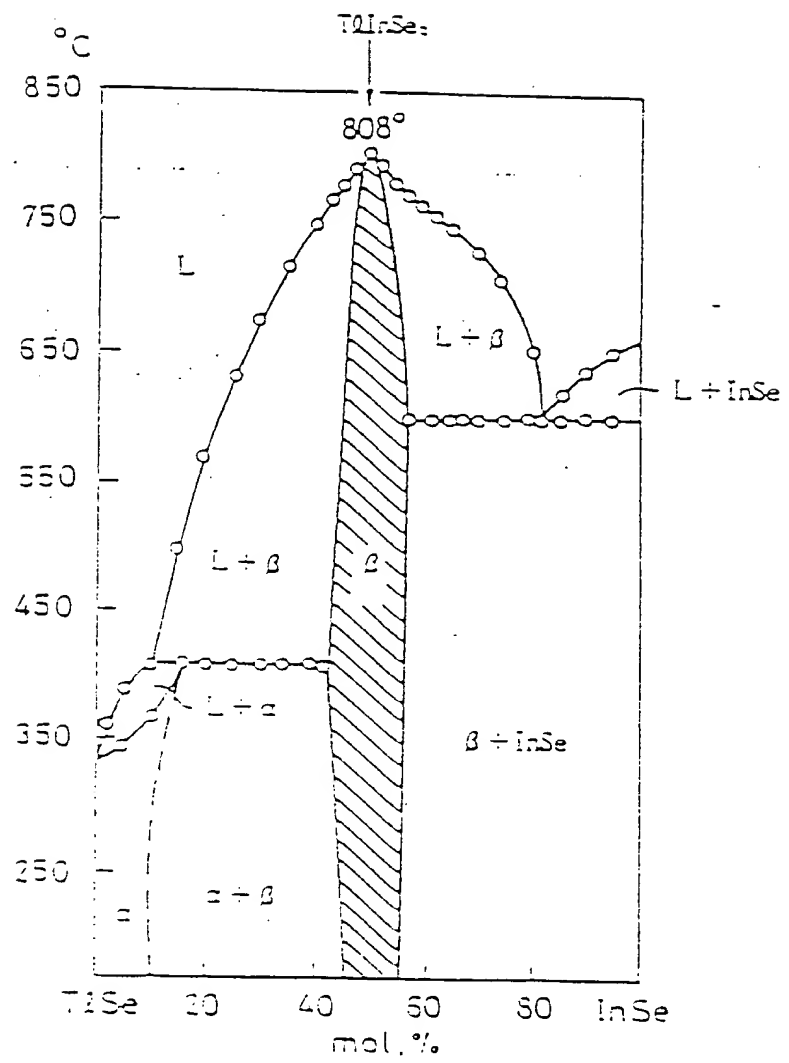


Fig. 30

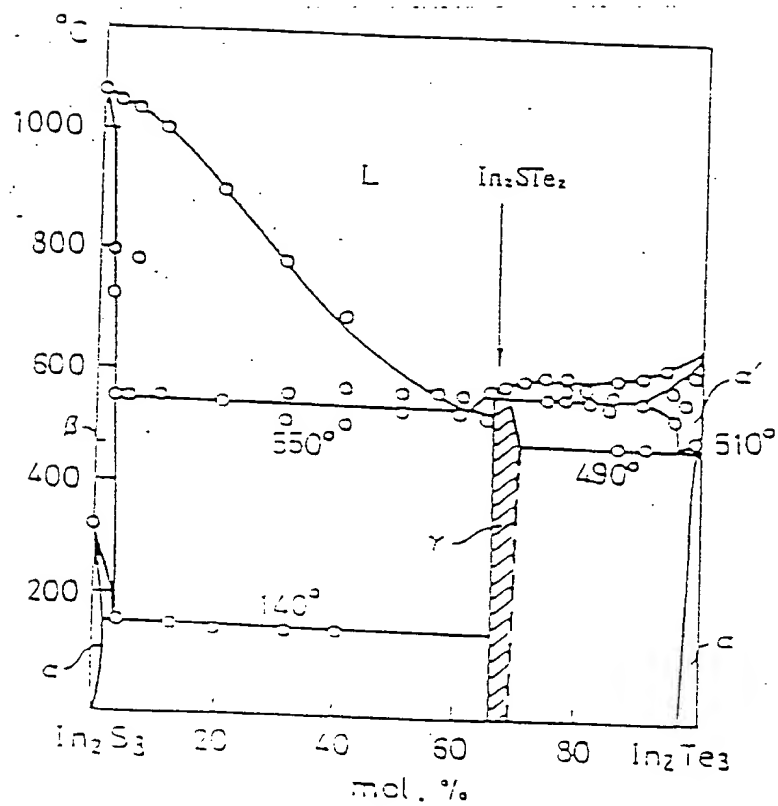


Fig. 31

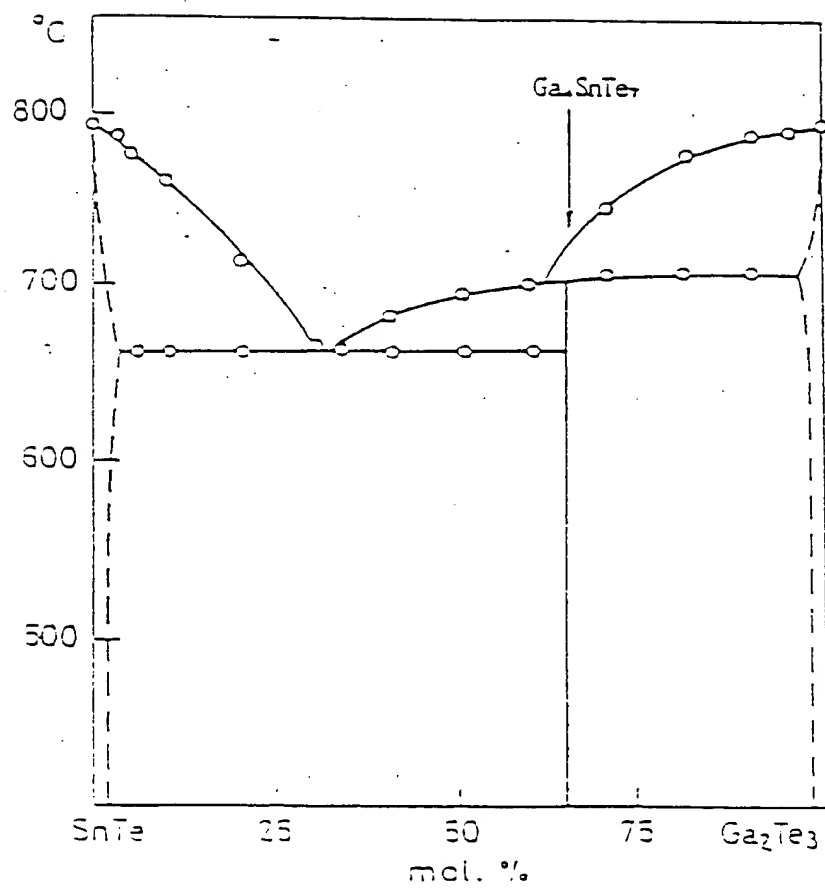




Fig. 32

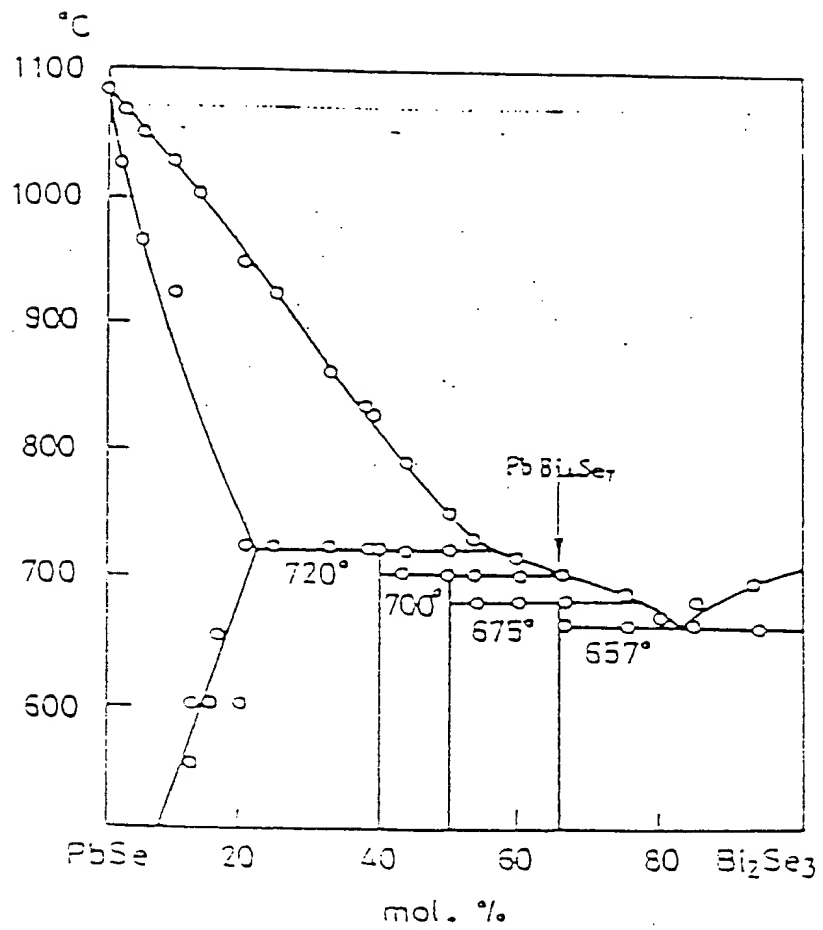


Fig. 33

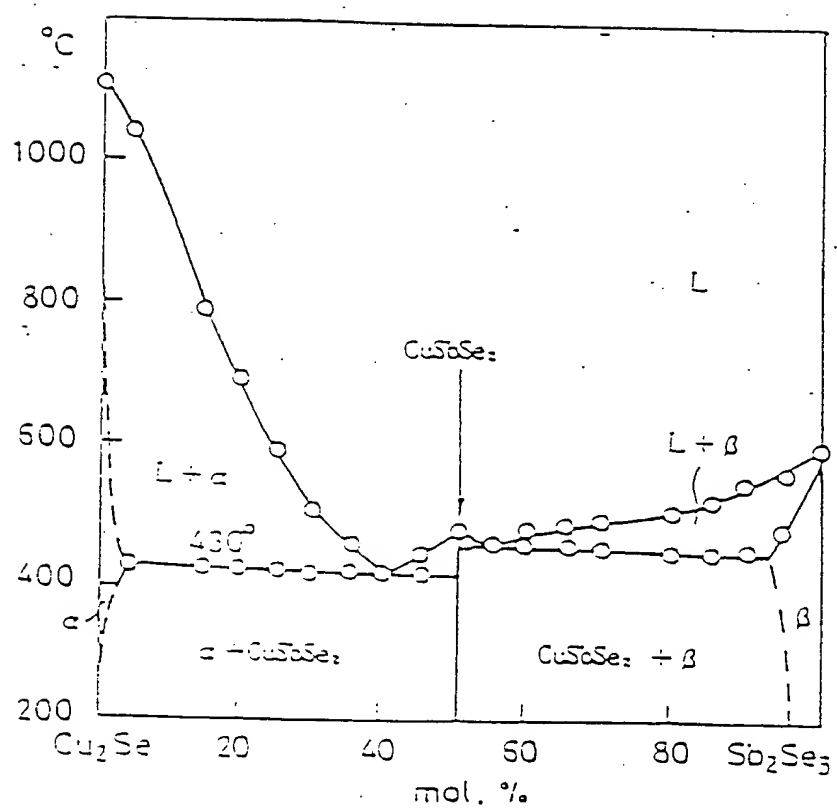


Fig. 34

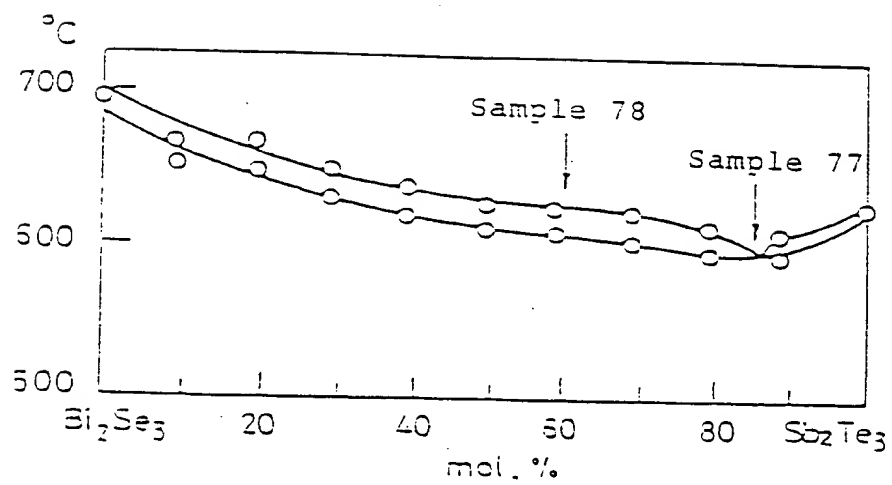


Fig. 35

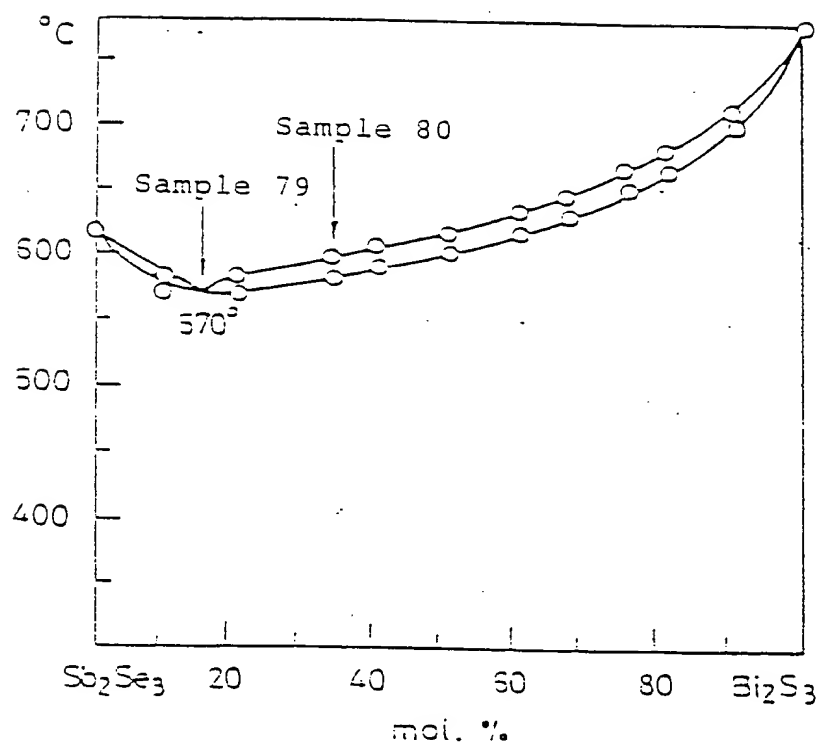


Fig. 36

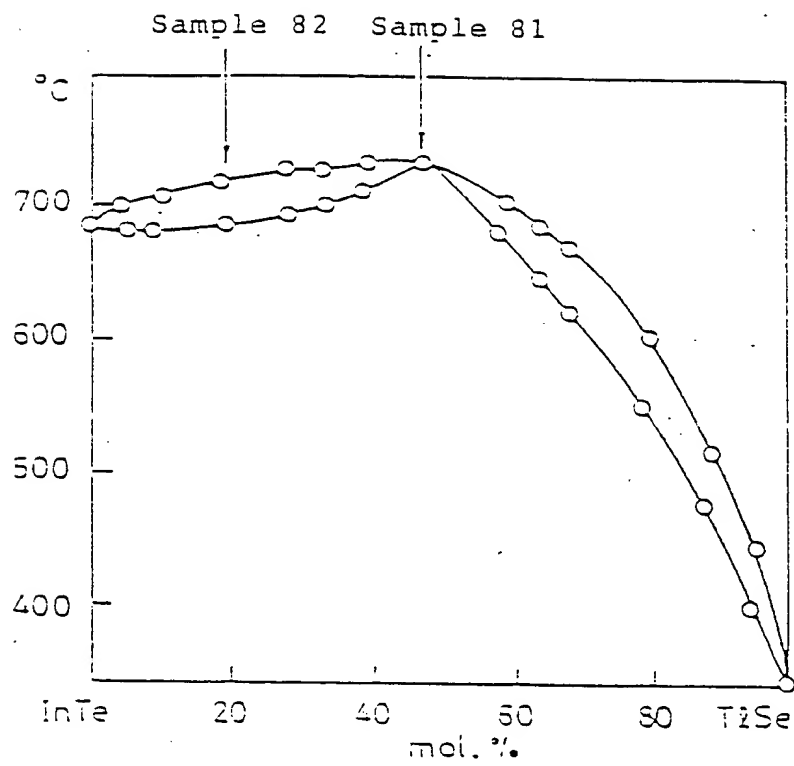


Fig. 37

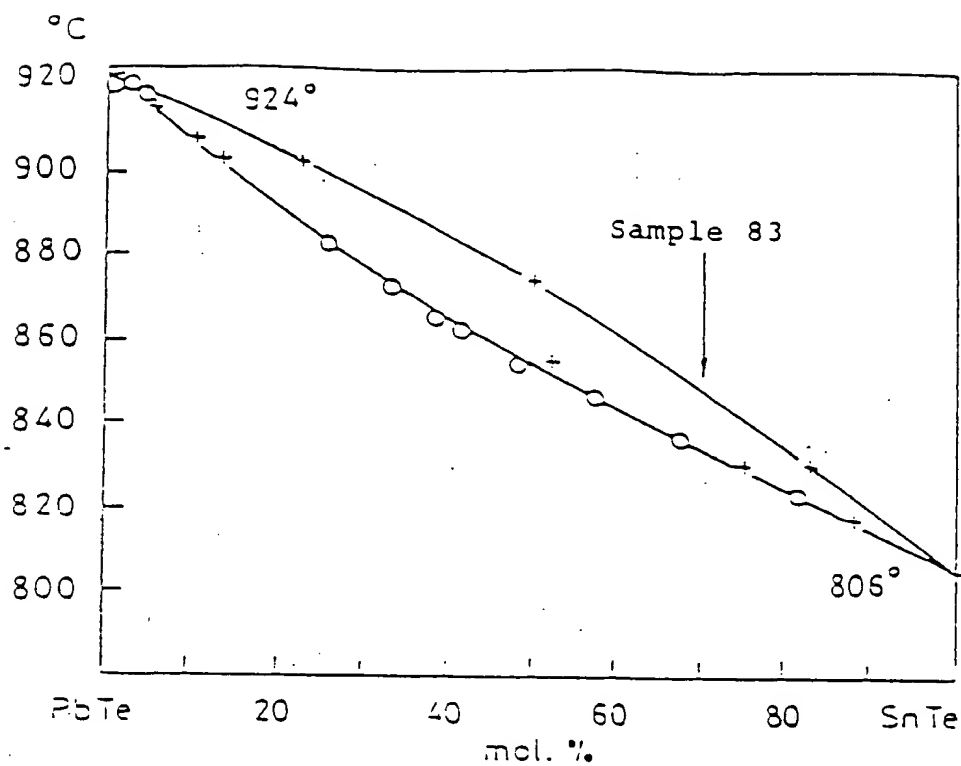


Fig. 38

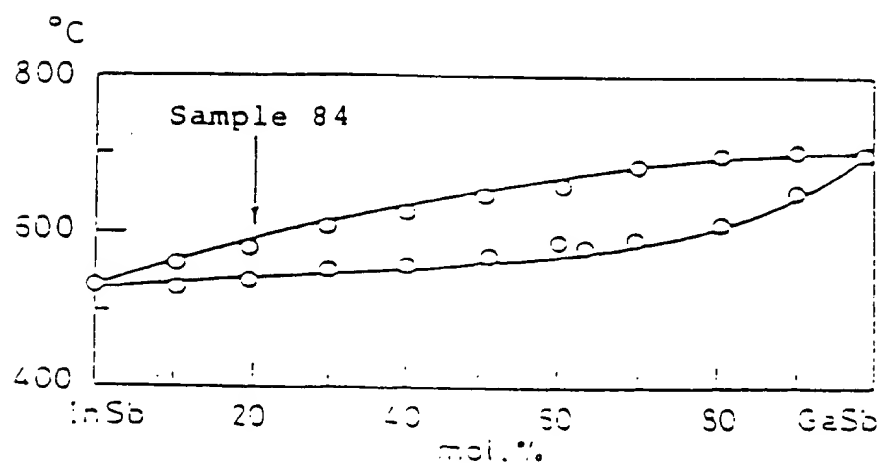


Fig. 39

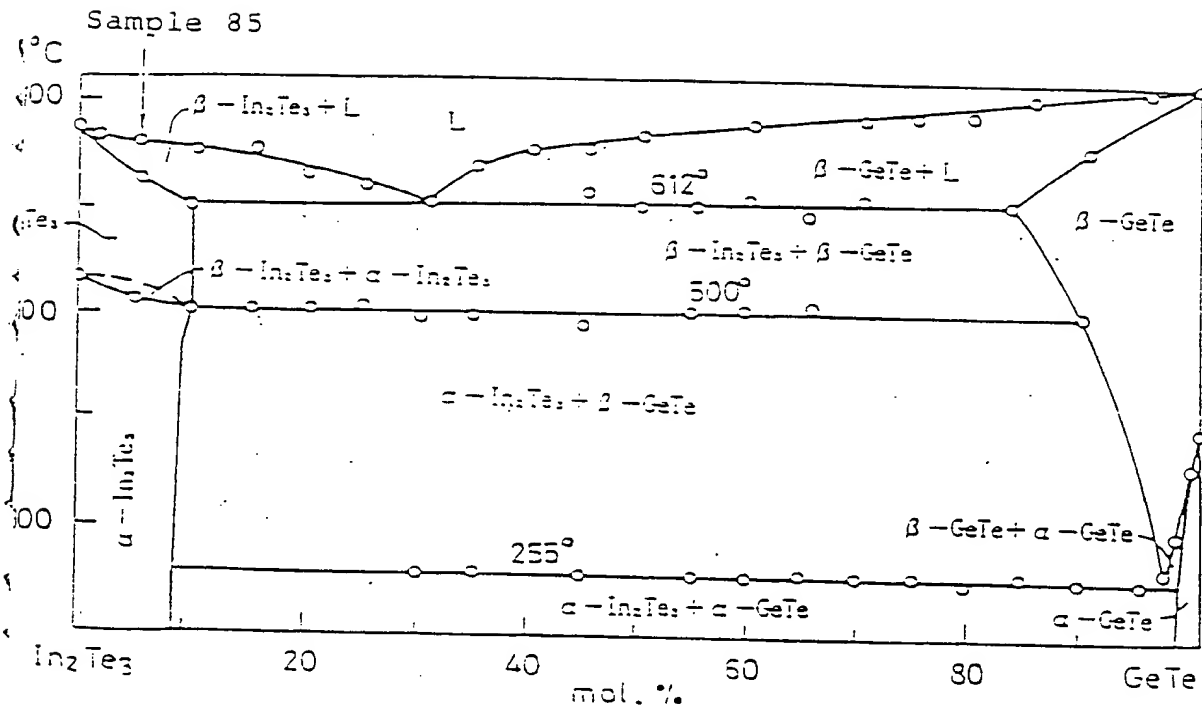
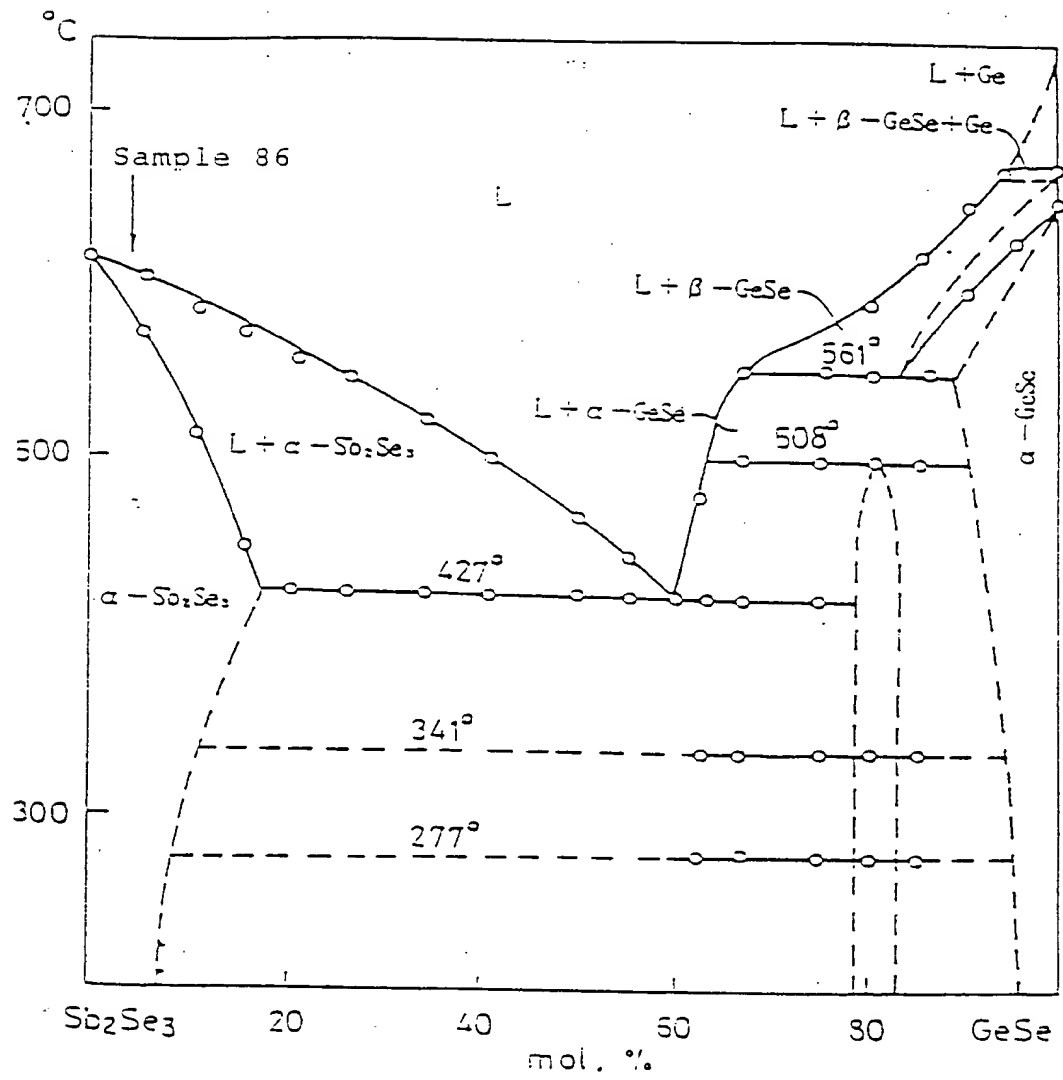
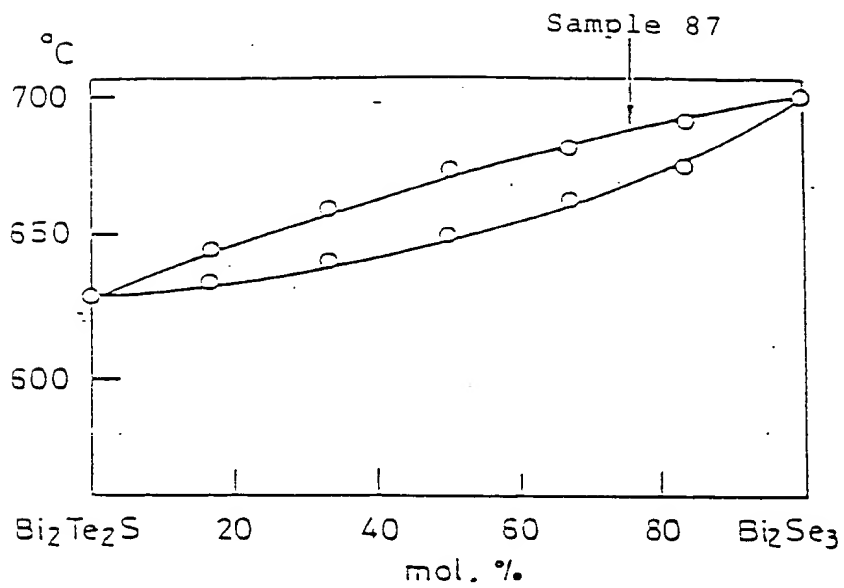


Fig. 40





Sample 41





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 387 898 A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **90105008.8**

(51) Int. Cl.<sup>5</sup>: **G11B 7/24, G11B 7/26**

(22) Date of filing: **16.03.90**

(30) Priority: **17.03.89 JP 63444/89**  
**17.03.89 JP 63445/89**  
**17.03.89 JP 63446/89**  
**17.03.89 JP 63447/89**  
**30.03.89 JP 76637/89**

(43) Date of publication of application:  
**19.09.90 Bulletin 90/38**

(84) Designated Contracting States:  
**DE FR GB NL**

(88) Date of deferred publication of the search report:  
**09.01.91 Bulletin 91/02**

(71) Applicant: **FUJI XEROX CO., LTD.**  
**No. 3-5, Akasaka 3-chome**  
**Minato-ku Tokyo 107(JP)**

(72) Inventor: **Ueno, Osamu**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**  
Inventor: **Kobayashi, Hideo**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**  
Inventor: **Ueyanagi, Kiichi**  
**2274 Hongo**  
**Ebina-shi, Kanagawa(JP)**

(74) Representative: **Boeters, Hans Dietrich, Dr. et al**  
**Boeters & Bauer Patentanwälte**  
**Bereiteranger 15 15**  
**D-8000 München 90(DE)**

(54) **Optical recording medium.**

(57) An optical recording medium comprising a substrate having provided thereon a layer of a recording material whose optical properties reversibly change on application of light, heat, etc., to conduct recording, reproduction, or erasure of information is disclosed, wherein the recording material has a composition (i) to (vii) containing three or more kinds of elements specified in the specification. The optical recording material of the invention is capable of conducting rewriting of information at an increased speed and stably maintaining the recorded information for an extended period of time.

**EP 0 387 898 A3**



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90105008.8

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	EP - A2 - 0 294 174 (EASTMANN KODAK CO.) * Fig. 7; claims 1,2 *	1	G 11 B 7/24 G 11 B 7/26
A	EP - A2 - 0 294 173 (EASTMAN KODAK CO.) * Fig. 7; claims 1-3 *	1	
A	EP - A2 - 0 286 406 (HITACHI, LTD.) * Fig. 8-10, 12-24 *	1	
A	EP - A2 - 0 278 790 (EASTMAN KODAK CO.) * Fig. 5; abstract *	1	
A	EP - A2 - 0 278 789 (EASTMAN KODAK CO.) * Fig. 7; abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			G 11 B 7/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 24-07-1990	Examiner BERGER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	